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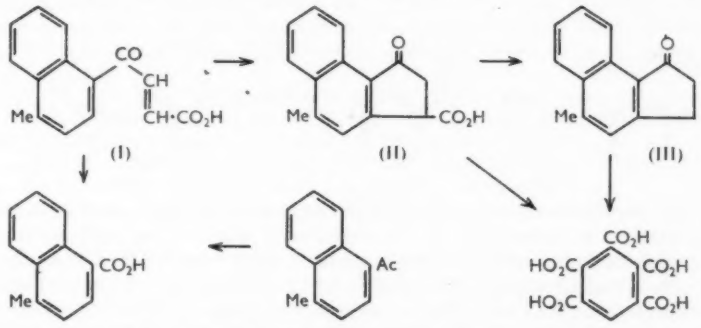
495. *Reaction of* 1- *and* 2-*Methylnaphthalene with Maleic Anhydride.*

By S. M. Makar, H. F. Bassilios, and A. Y. Salem.

1- and 2-Methylnaphthalene react with maleic anhydride in ethylene chloride and in absence of excess of aluminium chloride to give methylnaphthoylacrylic acids which are cyclised in molten aluminium chloride–sodium chloride at 100—120° by addition of the double bond to the naphthalene nucleus. The structure of the cyclised acids was established, and an easy and reliable method for oxidation of naphthalene derivatives to the carboxylic acids is described.

Naphthalene reacts with maleic anhydride in presence of anhydrous aluminium chloride,[1] yielding β-1- and β-2-naphthoylacrylic acid which readily cyclise, in presence of excess of aluminium chloride, to 3-oxo-4 : 5-benzindane-1-carboxylic and 1-oxo-4 : 5-benzindane-3-carboxylic acid respectively by addition of the double bond to the 2-position in the former and to the 1-position in the latter case. The present paper extends these results to two methylnaphthalenes. 1-Methylnaphthalene with a solution of the 1 : 2 maleic anhydride–aluminium chloride complex in ethylene dichloride readily affords β-(4-methyl-1-naphthoyl)acrylic acid (I) in a good yield. This acid is golden-yellow and decolorises dilute potassium permanganate solution and bromine in carbon tetrachloride. It provides 4-



methyl-1-naphthoic acid on oxidation with cold neutral permanganate solution, identical with that obtained by hypochlorite oxidation of 1-acetyl-4-methylnaphthalene. The acid (I) is cyclised in molten aluminium–sodium chloride at 100—120° to a saturated acid, which is proved to be 6-methyl-3-oxo-4 : 5-benzindane-1-carboxylic acid (II) by permanganate oxidation to benzenepentacarboxylic acid and not the tetracarboxylic acid, and by decarboxylation in quinoline in presence of copper chromite to 6-methyl-4 : 5-benzindan-3-one [2] (III). The indanone also affords benzenepentacarboxylic acid on permanganate oxidation.

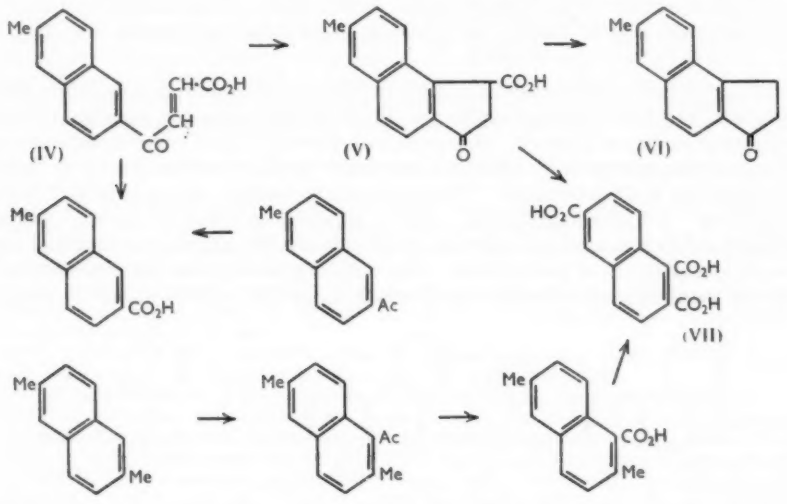
Similarly, β-(6-methyl-2-naphthoyl)acrylic acid (IV) was obtained from 2-methylnaphthalene, but the crude product was a yellow sticky solid, probably owing to the presence of an isomeric acid. Crystallisation from benzene or acetic acid provided the pure acid (IV) in *ca.* 48% yield as golden-yellow needles, m. p. 169—170°. No isomer could be obtained from the mother-liquor, and permanganate oxidation gave only one methylnaphthoic acid.

β-(6-Methyl-2-naphthoyl)acrylic acid (IV) in molten sodium–aluminium chloride at 100—120° affords 3′-methyl-1-oxo-4 : 5-benzindane-3-carboxylic acid (V), oxidised by

[1] Baddeley, Makar, and Ivinson, *J.*, 1952, 3605.
[2] Mayer, Fritz, and Müller, *Ber.*, 1927, **60**, 2278.

nitric acid to naphthalene-1 : 2 : 6-tricarboxylic acid (VII). This acid is new, so it was prepared for comparison from 2 : 6-dimethylnaphthalene by acetylation in presence of aluminium chloride. The 1-acetyl-2 : 6-dimethylnaphthalene, thus obtained, was oxidised to the monocarboxylic acid by hypochlorite and thence by nitric acid to the previously obtained naphthalene-1 : 2 : 6-tricarboxylic acid.

Oxidation of alkyl and other side-chains in a naphthalene compound by nitric acid offers an easy and reliable method for production of naphthalenecarboxylic acids which have hitherto been difficult to prepare: mild oxidising agents such as potassium ferri-



cyanide react slowly and give poor yields of the carboxylic acid; strong oxidising agents such as potassium permanganate or chromic acid break the naphthalene nucleus. The procedure provided the corresponding naphthoic acid from 1- or 2-methylnaphthalene and the corresponding dicarboxylic acid from 2 : 6-dimethyl-, 1-acetyl-4-methyl-, and 2-acetyl-6-methyl-naphthalene. The known procedure for oxidation of benzene derivatives to benzenepolycarboxylic acids by nitric acid could not be applied to naphthalene derivatives (to give benzenepolycarboxylic acids by fission of the naphthalene nucleus); the product is frequently a polymer of a nitrated naphthalene derivative.

Like other oxo-4 : 5-benzindanecarboxylic acids, 3'-methyl-1-oxo-4 : 5-benzindane-3-carboxylic acid (V) is decarboxylated to 3'-methyl-1-oxo-4 : 5-benzindane (VI) in hot quinoline in presence of copper chromite.

Experimental

Analyses are by M. Sobotka, Graz, Austria.

β-(*4-Methyl-1-naphthoyl*)*acrylic Acid* [*4-(4-Methyl-1-naphthyl)-4-oxobut-2-enoic Acid*].—Finely powdered aluminium chloride (60 g.) was gradually added to a stirred solution of maleic anhydride (24·5 g.) in anhydrous ethylene chloride (250 c.c.), and the mixture stirred for 0·5 hr. at room temperature. The resulting solution was then gradually decanted from undissolved aluminium chloride into a solution of 1-methylnaphthalene (35·5 g.) in ethylene chloride (100 c.c.). Reaction was instantaneous and the mixture, after 0·5 hr. at room temperature, was poured on ice and dilute hydrochloric acid. The organic solvent was removed by distillation and the yellow sticky residue, which solidified overnight, was separated, washed with water and dried under reduced pressure. Crystallisation from benzene provided β-(*4-methyl-1-naphthoyl*)-*acrylic acid* (41 g.) as golden-yellow needles, m. p. 179—180° (Found: C, 75·2; H, 5·3%; equiv.,

239. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%; equiv., 240). It afforded 4-methyl-1-naphthoic acid,[3] m. p. 174—175°, on oxidation with 0·1N-potassium permanganate in presence of 2N-sodium carbonate. The melting point was not depressed on admixture with 4-methyl-1-naphthoic acid obtained by oxidation of 1-acetyl-4-methylnaphthalene[4] with sodium hypochlorite.

β-(6-*Methyl*-2-*naphthoyl*)*acrylic Acid* [4-(6-*Methyl*-2-*naphthyl*)-4-*oxobut*-2-*enoic Acid*].—This *acid* was the only identifiable product obtained from the interaction of 2-methylnaphthalene (1 mole) with maleic anhydride (1 mole) and aluminium chloride (2 moles) by the above procedure. The crude yellow sticky material (A) crystallised from acetic acid or 30 : 70 benzene–chloroform as golden-yellow needles, m. p. 169—170° (48% yield) (Found: C, 74·9; H, 5·2%; equiv., 240). Oxidation with cold potassium permanganate solution provided 6-methyl-2-naphthoic acid[5] which crystallised from acetic acid in colourless needles, m. p. and mixed m. p. 229—230°.[5]

Fractional crystallisation of a product (B) recovered from the mother-liquor of (A) by using acetic acid, chloroform, ethylene chloride, or ethanol provided in each case only impure samples of the same acrylic acid. Oxidation of product (B) with cold potassium permanganate solution provided an impure 6-methyl-2-naphthoic acid. Crystallisation of the semicarbazone also led to the same acrylic acid.

Isomerisation of β-(4-*Methyl*-1-*naphthoyl*)*acrylic Acid*.—This acid (12 g.) was gradually introduced into molten aluminium chloride (120 g.) and sodium chloride (18 g.) at 100—120°. The mixture was poured, after 1 hr., on ice and dilute hydrochloric acid. The pale brown product crystallised from acetic acid (charcoal), to give 6-*methyl*-3-*oxo*-4 : 5-*benzindane*-1-*carboxylic acid* (II) (8·2 g.) as pale yellow needles, m. p. 210° (Found: C, 75·0; H, 5·2%; equiv., 240. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%; equiv., 240). Oxidation of this acid with boiling potassium permanganate solution in presence of sulphuric acid afforded benzenepentacarboxylic acid, m. p. and mixed m. p. 225—230° (decomp.) (pentamethyl ester,[6] m. p. and mixed m. p. 145—147°).

The acid (II) was decarboxylated by copper chromite in quinoline at 170—180°; the catalyst was removed by filtration, quinoline was separated by extraction with acid, and the residue was distilled with steam. It afforded 6-methyl-4 : 5-benzindan-3-one (III) as colourless needles,[7] m. p. 133—134° (Found: C, 85·8; H, 6·5. Calc. for $C_{14}H_{12}O$: C, 85·7; H, 6·1%) [*semicarbazone*, m. p. 266° (Found: N, 16·4. $C_{15}H_{15}ON_3$ requires N, 16·6%)]. This indanone also provided benzenepentacarboxylic acid on vigorous oxidation with acid permanganate solution.

Isomerisation of β-(6-*Methyl*-2-*naphthoyl*)*acrylic Acid*.—By the procedure described above, this acid (10 g.) afforded 3′-methyl-1-oxo-4 : 5-benzindane-3-carboxylic acid (6·7 g.) which crystallised from acetic acid in pale yellow prisms, m. p. 204—205° (Found: C, 75·0; H, 5·3%; equiv., 239). It formed a 2 : 4-dinitrophenylhydrazone, did not decolorise cold permanganate or bromine in carbon tetrachloride, and was oxidised by 8% nitric acid solution (w/v) in a sealed tube at 150° to 1 : 2 : 6-*naphthalenetricarboxylic acid* (VII), m. p. and mixed m. p. 298—300° (decomp.) (Found: C, 60·3; H, 3·2%; equiv., 87. $C_{13}H_8O_6$ requires C, 60·0; H, 3·0%, equiv., 86·7). The *trimethyl ester* (prepared by ethereal diazomethane) crystallised from methanol in needles, m. p. and mixed m. p. 139—140° (Found: C, 63·5; H, 5·0. $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·7%). The authentic samples of 1 : 2 : 6-naphthalenetricarboxylic acid and its trimethyl ester were prepared by acetylation of 2 : 6-dimethylnaphthalene.[8] The 1-acetyl-2 : 6-dimethylnaphthalene, m. p. 71—72° (picrate, m. p. 139—140°; semicarbazone, m. p. 193—194°), thus obtained was oxidised by sodium hypochlorite solution to 2 : 6-dimethyl-1-naphthoic acid which crystallised from acetic acid in colourless needles,[9] m. p. 203—204°. Oxidation of this acid with 8% nitric acid at 150° afforded the required tricarboxylic acid.

[3] Mayer and Sieglitz, *Ber.*, 1922, **55**, 1839.
[4] Dziewonski and Mahusinska, *Bull. intern. Acad. polon., A*, 1938, 316; *Brit. Chem. Abs.*, 1939, *A* (II), 23.
[5] Kon and Weller, *J.*, 1939, 792.
[6] Ruzicka and Rudolph, *Helv. Chim. Acta*, 1927, **10**, 919; Jacobsen, Stromberg, and Peterson, *J. Amer. Chem. Soc.*, 1949, **71**, 1384; Fleischer and Retze, *Ber.*, 1923, **56**, 228.
[7] Mayer, Fritz, and Müller, *Ber.*, 1927, **60**, 2278.
[8] Clar, Wallenstein, and Avenarius, *Ber.*, 1929, **62**, 950; Dziewonski, Stec, and Zagala, *Bull. intern. Acad. polon., A*, 1928, 324.
[9] Lesser and Gad, *Ber.*, 1927, **60**, 244.

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It was also obtained by direct oxidation of 1-acetyl-2 : 6-dimethylnaphthalene with 8% nitric acid.

Like other indanonecarboxylic acids,[10] 3′-methyl-1-oxo-4 : 5-benzindane-3-carboxylic acid (V) was decarboxylated by copper chromite in quinoline; it gave *3′-methyl-4 : 5-benzindane-3-one* which crystallised from hot water in colourless needles, m. p. 112—113° (Found: C, 85·6; H, 6·4%) [semicarbazone, m. p. 276° (decomp.) (Found: N, 16·1%)].

CHEMICAL TECHNOLOGY DEPARTMENT, FACULTY OF ENGINEERING, ALEXANDRIA UNIVERSITY, ALEXANDRIA, EGYPT. [*Received, December 23rd*, 1957.]

[10] Baddeley and Makar, *J.*, 1952, 3289, 3605.

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496. *The Absorption Spectra of Nitrous Acid in Aqueous Perchloric Acid.*

By C. A. BUNTON and G. STEDMAN.

Ultraviolet-absorption measurements show that with increasing acidity, molecular nitrous acid, HNO_2, is protonated and dehydrated. The visible-absorption spectra indicate that appreciable amounts of dinitrogen trioxide, N_2O_3, may be present.

PHYSICAL measurements on solutions of " nitrous acid " in aqueous mineral acids show that, in dilute acidic media, " nitrous acid " (by which is meant all the species which are analysed as nitrite on dilution with water) exists as molecular nitrous acid, HNO_2.[1-3] With increasing acidity this is protonated and dehydrated, and in concentrated sulphuric acid the nitrosonium ion, NO^+, is the only entity of importance.[4] There is kinetic evidence for the existence of this ion, and of the nitrous acidium ion, $H_2NO_2^+$, and of dinitrogen trioxide, as intermediates in reactions of " nitrous acid," [5] and the present work was intended to give physical information on the existence of dinitrogen trioxide in acid solutions. Some of our results on the ultraviolet absorption spectra are shown in Table 1 (cf. refs. 1 and 2). In perchloric acid solutions less than *ca.* 7M the spectrum is that of molecular nitrous acid, and very similar to those of alkyl nitrites in organic solvents [6] and of a gaseous mixture of nitrogen dioxide, nitric oxide, and water.[7] For " nitrous acid " of <0·05M-concentration the Beer–Lambert law was obeyed in this region. Addition of sodium nitrate, in amount comparable with that of the nitric acid which could be formed by decomposition of " nitrous acid " during preparation of the solution, had little or no effect on the absorption. Species formed by interaction of " nitrous " and nitric acid therefore do not affect these spectra, which are those of molecular nitrous acid.

In accord with the observations of other workers,[1-3] we find that increase of acidity changes the spectra completely: the fine structure of the absorption band of nitrous acid is replaced by a band rising towards shorter wavelengths.

The molecular extinction coefficients in this wavelength range (3300—3600 Å) in 8—10M-perchloric acid (Table 1) cannot easily be accounted for in terms of molecular nitrous acid and the nitrosonium ion (the spectrum in sulphuric acid being assumed to be that of NO^+) unless there is a very large wavelength shift in the absorption of the nitrosonium ion when the concentrated mineral acid is diluted with water. Bayliss and Watts [2]

[1] Singer and Vamplew, *J.*, 1956, 3971.
[2] Bayliss and Watts, *Chem. and Ind.*, 1955, 1353; *Austral. J. Chem.*, 1956, **9**, 319.
[3] Deschamps, *Compt. rend.*, 1957, **245**, 1432.
[4] Angus and Leckie, *Proc. Roy. Soc.*, 1935, *A*, **149**, 327; 1935, *A*, **150**, 615; Gillespie, Graham, Hughes, Ingold, and Peeling, *J.*, 1950, 2504; Millen, *J.*, 1950, 2600.
[5] Abel, Schmidt, and Schrafonik, *Z. phys. Chem.*, 1931, **148**, 510; Hughes, Ingold, and Ridd, *J.*, 1958, 58, 65, 77, 88; Bunton, Llewellyn, and Stedman, *Nature*, 1955, **175**, 83.
[6] Tarte, *J. Chem. Phys.*, 1952, **20**, 1570; Banus, *J.*, 1953, 3755; Haszeldine and Mattinson, *ibid.*, 1955, 4172.
[7] Porter, *J. Chem. Phys.*, 1951, **19**, 1278.

find a large shift when 98% sulphuric acid is diluted with water, and they suggest that an additional species, the nitrous acidium ion, exists in appreciable quantities in aqueous sulphuric, hydrochloric, and phosphoric acid. Singer and Vamplew [1] observed only a

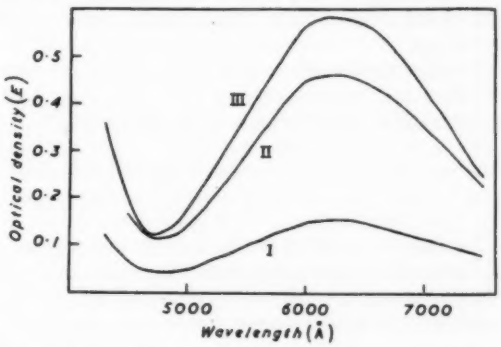
TABLE 1. *Effect of acid concentration upon the ultraviolet absorption spectra of nitrous acid.*

Solute: sodium nitrite unless otherwise stated.
Absorption maxima italicised: minima in parentheses.

$HClO_4$ (M)	ε_{3300}	ε_{3460}	ε_{3500}	ε_{3560}	ε_{3630}	ε_{3690}	ε_{3780}	ε_{3830}
0·8 [a]	—	*39*	(35)	*56*	(39)	*57*	(26)	*34*
5·1	22	*43*	(41)	*59, 60* [b]	(42)	*61, 62* [b]	(31)	*37, 36* [b]
6·75	70	49	(47)	*56*	(40)	*50*	(26)	*28*
8·0 [c]	182	62	—	29	—	18	—	6
10·0	261	88	—	28	—	9	—	—
98% H_2SO_4	6	3	—	—	—	—	—	—

[a] Addition of sodium perchlorate (6M) to this solution shifts the maxima to slightly shorter wavelengths. [b] These values were obtained with nitrosyl perchlorate (0·02M). [c] A solution of sodium nitrite in a mixture of perchloric acid (7·42M) and sulphuric acid (5·35M) gave slightly lower values of ε.

small wavelength shift when 60% perchloric acid was diluted with water and found no evidence for this additional species. Our results do not differentiate between these two possibilities, although they confirm the view that the Beer–Lambert law is obeyed, and



Visible spectra in 6·9M-perchloric acid. Nitrite = (I) 0·064M, (II) 0·124M, (III) 0·141M (d = 4 *cm.*).

the absorbing species therefore contains one equivalent of nitrite per mole. Bayliss and Watts show that the ratio of supposed nitrous acidium ion to nitrous acid, determined indirectly by spectrophotometry, varies linearly with the activity of sulphuric acid. Their results can be fitted equally well to a near-linear variation with the Hammett acidity function, h_0, which measures the ability of an acidic solution to protonate a neutral base.

Addition of sodium perchlorate slightly increases the absorption in the region 3300—3500 Å (although its effect is partially masked because increase in ionic concentration decreases the fine structure of the absorption). This is because addition of this salt increases the protonating power of the medium,[8] with consequent conversion of molecular nitrous acid into its protonated and dehydrated derivatives. Addition of large (*ca.* 0·5M) amounts of sodium nitrate increases the absorption over the wavelength range 3000—4000 Å, presumably by formation of dinitrogen tetroxide–nitrogen dioxide.

If the concentration of " nitrous acid " is greater than *ca.* 5×10^{-2}M the Beer–Lambert law is no longer obeyed; examples are given in Table 2. There is no increased absorption below 3500 Å, and the increase above 3500 Å is not caused by formation of the nitrosonium or nitrous acidium ion. We suppose it to be caused by dinitrogen trioxide. This conclusion is supported by examination of the visible absorption spectra (Figure). These spectra

[8] Long and Paul, *Chem. Rev.*, 1957, **57**, 1.

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are characterised by a broad absorption maximum at 6250 Å, which can only be that of dinitrogen trioxide because, although nitrogen dioxide absorbs in the visible region, its absorption overlapping that of dinitrogen trioxide,[9] the ratios of optical densities, for fixed " nitrous acid " concentrations, at various wavelengths are independent of solvent composition. Data illustrating this are shown in the Experimental section. This test

TABLE 2. *Variation of extinction coefficient with concentration of " nitrous acid."* $[HClO_4] = 5{\cdot}1$M.

[Nitrite] (M)	ε_{3330}	ε_{3690}	ε_{3500}
0·0208	35·5	62·0	60·2
0·0721	38·1	66·7	66·9
0·151	39·7	69·5	77·2

shows that despite marked changes in the nitrous acid species present, the visible absorption spectrum is that of one species only. Similar behaviour is shown in aqueous sulphuric acid.

Our assumption on the nature of this visible absorption is supported by comparison with the absorption spectra of various *N*-nitroso-compounds.[6] Confirmation comes from a recent demonstration by Dr. Joan Mason[10] that dinitrogen trioxide in toluene has a visible absorption spectrum with $\lambda_{max.}$ 6620 Å (with a half-band width similar to that observed here) and $\varepsilon_{max.}$ 19. If we assume that this value for the molar extinction coefficient in toluene can be used for measurements in perchloric acid we calculate that up to 15% of the " nitrous acid " can exist as dinitrogen trioxide (with $HClO_4$ 6·75M, and nitrite *ca.* 0·15M).

Further confirmation that dinitrogen trioxide exists in appreciable amounts in these perchloric acid solutions comes from the variation of the optical density, E_{6250}, with nitrite concentration; this, for a given perchloric acidity, fits the empirical equation:

$$\log E_{6250} = n \log [\text{nitrite}] + \log C,$$

i.e.,

$$E_{6250} = C[\text{nitrite}]^n$$

Values of n and C have been tabulated for various solvent compositions (Table 3), on the basis of data illustrated in the Experimental section. For a given nitrite concentration, with increasing perchloric acid concentration, E_{6250} first increases (up to 6·7M), then decreases. Values of n show a converse behaviour.

TABLE 3. *Empirical relation between optical density and nitrous acid concentration.*

$[HClO_4]$ (M)	4·2	5·1	6·1	6·75	7·2	7·6
n	1·84	1·72	1·73	1·64	1·70	1·82
C	3·2	7·4	16·6	10·8	4·5	1·1
10^3K_e (mole^{-1} l.)	5·7	19	49	56	29	36

The increase in E_{6250} corresponds to an increasing dehydration of molecular nitrous acid by the reaction, $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$. When molecular nitrous acid is the bulk component, the concentration of dinitrogen trioxide should follow the relation:

$$[N_2O_3] = K_{N_2O_3}[HNO_2]^2 f^2_{HNO_2}/a_{H_2O} \cdot f_{N_2O_3}$$

The activity coefficient of nitrous acid, f_{HNO_2}, increases with increasing ionic strength,[11] and the activity of water, a_{H_2O}, decreases with increasing acidity.[12] Therefore the concentration of dinitrogen trioxide, and E_{6250}, should increase with increasing perchloric acidity and be proportional to $[\text{nitrite}]^2$, *i.e.*, $n = 2$ when $[HNO_2] \approx [\text{nitrite}]$.

[9] Berl and Winnaker, *Z. anorg. Chem.*, 1933, **212**, 113; Vodar, *Compt. rend.*, 1937, **204**, 1467.
[10] J. Mason, personal communication.
[11] Abel and Neusser, *Monatsh.*, 1929, **53/54**, 855.
[12] Robinson and Baker, *Trans. Proc. Roy. Soc., N.Z.*, 1946, **76**, (II), 250.

This is found at low perchloric acid concentrations, but with increasing perchloric acidity the amount of dinitrogen trioxide increases sufficiently for the amount of molecular nitrous acid to be less than the amount of analytical nitrite, and n will then become less than 2. (In the hypothetical case of complete dehydration to dinitrogen trioxide, N_2O_3, n would equal 1.)

With further increase in perchloric acid concentration both molecular nitrous acid and dinitrogen trioxide are converted into the nitrosonium and possibly nitrous acidium ion by the reactions:

$$HNO_2 + H^+ \rightleftharpoons H_2NO_2^+$$

and

$$H_2NO_2^+ \rightleftharpoons NO^+ + H_2O$$

or

$$H_2NO_2^+ + NO_2^- \rightleftharpoons N_2O_3 + H_2O$$

and

$$N_2O_3 + 2H^+ \rightleftharpoons 2NO^+ + H_2O$$

In the region where these ions are the predominant species ($HClO_4 > 8$M) the absorption at 6250 Å will decrease and n will increase towards 2 with increasing concentration of perchloric acid. Hence dehydration of nitrous acid to dinitrogen trioxide and conversion into the nitrosonium, and possibly the nitrous acidium, ion, occur within the range of perchloric acid concentrations studied, the concentration of these species depending in a predictable manner upon the ionic concentration of the medium. It is possible that some of the apparent discrepancies between ultraviolet absorption measurements in perchloric and sulphuric acid [1,2] may be due to neglect of the possible presence of dinitrogen trioxide in some of the solutions.

It is possible to calculate a classical equilibrium constant, $K_c = [N_2O_3]/[HNO_2]^2$ for the dehydration of nitrous acid. The concentrations of dinitrogen trioxide are from the present work, and those of molecular nitrous acid are calculated from the proportions of nitrous acid and stoicheiometric nitrite determined by Singer and Vamplew.[1] We assume that these proportions of species which contain one equivalent of nitrite per mole will change little with changing nitrite concentration. The values of K_c are tabulated with those of the empirical coefficient C (Table 3). They are independent of the source and concentration of the "nitrous acid". They increase with increasing perchloric acidity (and decreasing water activity [12] up to *ca.* 7M. Above this, ionic species derived from nitrous acid become important,[1,2,4] and K_c falls slightly.

Experimental

Preparation of Solutions.—Solutions of nitrous acid in aqueous perchloric acid were made up by adding sodium nitrite or nitrosyl perchlorate to the aqueous acid. Allowance was made for the removal of protons by the nitrite ion where this would significantly affect the perchloric acid concentration. The nitrous acid concentration was estimated colorimetrically after addition of a sample to excess of alkali. Solutions were covered with a layer of spectroscopically pure hexane to decrease the decomposition of nitrous acid during spectral measurements; all measurements were made as rapidly as possible. Where the decomposition rate was high ($[HNO_2] > ca.$ 0·1M), successive readings of optical density were taken at regular intervals, and extrapolated back to the time of analysis of the nitrous acid.

The ionic strength of the medium, and hence its protonating and dehydrating power, will depend upon the form in which the nitrous acid is added, *i.e.*, as sodium nitrite or nitrosyl perchlorate. This may affect the quantitative significance of the results with the more concentrated solutions of nitrous acid.

Determination of Optical Densities.—Spectra were measured on a Unicam S.P. 500 spectrophotometer, at room temperature, with matched stoppered cells of glass for the visible, and fused silica for the ultraviolet, region.

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The independence of the ratio, E_{6250}/E_{7500}, of concentration and environment is shown in Tables (cell length 4 cm.).

Variation of nitrous acid, $[HClO_4] = 6{\cdot}9$M.

[Nitrite] (M)	0·0639	0·124		0·141	0·0734[a]	0·0834[b]
E_{6250}/E_{7500}	2·08	2·16	2·13	2·15	2·08	2·17

[a] $[NaClO_4] = 1{\cdot}64$M. [b] $[NaNO_3] = 1{\cdot}07$M.

Variation of perchloric acid.

$[HClO_4] = 4{\cdot}2$M: E_{6250}/E_{7500} (mean) = 2·03.
$[HClO_4] = 8{\cdot}0$M: E_{6250}/E_{7500} (mean) = 2·18.

The authors are indebted to Drs. J. Mason and J. M. Deschamps for valuable discussions, and to the D.S.I.R. for a grant (to G. S.).

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497. *Sodium Derivatives of Stannane.*

By H. J. EMELÉUS and S. F. A. KETTLE.

Conductometric titration of a solution of sodium in liquid ammonia with stannane shows the formation of stannylsodium (sodiostannane), SnH_3Na, and stannylenedisodium (disodiostannane), SnH_2Na_2. The former decomposes at −63·5° in absence of ammonia, but reacts in ammonia solution with alkyl iodides to form alkyl stannanes, and with ammonium chloride to form stannane. Stannylenedisodium is fairly stable at 0° in absence of ammonia. In ammonia solution it does not react with methyl iodide and, with ammonium chloride, gives stannane. An attempt to prepare plumbane, PbH_4, by the reduction of lead tetrachloride with lithium aluminium hydride yielded only metallic lead.

SODIUM derivatives of alkyl- and aryl-tin hydrides are formed by the reaction of sodium in liquid ammonia solution with organotin mono- and di-halides, or with the corresponding hydrides. The stability appears to be greatest with three alkyl or aryl groups in the molecule. Thus, both trimethyl- and triphenyl-stannylsodium are known in the solid state.[1] Dimethylstannylsodium is unknown and dimethylstannylenedisodium is known only as its deep red solution in liquid ammonia.[2] There has been no systematic search for compounds of the type $RSnH_2Na$ and SnH_3Na, notwithstanding the isolation of germanylsodium, GeH_3Na, as an ammine and the probable existence in ammonia solution of germanylenedisodium, GeH_2Na_2.[3] The ready decomposition of stannane at room temperature made it probable that stannylsodium, SnH_3Na, would, if it existed, be very unstable. Evidence for its existence was therefore sought by the conductometric titration with stannane of a solution of sodium in liquid ammonia. This method allowed the existence of one or more sodium derivatives at relatively low temperatures to be examined.

In a study of its kinetics, which will be published elsewhere, the decomposition of the gas was found to be completely inhibited by a small proportion of oxygen, which probably poisoned the tin surface on which the hydride is known to decompose catalytically. This finding greatly facilitated both the preparation and storage of stannane. The hydride also decomposed readily in presence of gaseous ammonia, so additions of stannane to ammonia solutions were made at low temperatures. Conductivity measurements were made at −63·5° (m. p. of chloroform) in a cell of conventional design. This was charged

[1] Kraus and Sessions, *J. Amer. Chem. Soc.*, 1925, **47**, 2361; Chambers and Scherer, *ibid.*, 1926, **48**, 1054.
[2] Kraus and Kahler, *ibid.*, 1933, **55**, 3537; Kraus and Johnson, *ibid.*, 1933, **55**, 3542.
[3] Kraus and Carney, *ibid.*, 1934, **56**, 765.

with a solution of sodium in ammonia, the conductivity of which was measured. Small successive additions of stannane were then made at liquid-nitrogen temperature and reaction was allowed to occur at −63·5°. The conductivity and hydrogen evolved were measured after each addition.

The typical titration curve (Fig. 1) was obtained with 0·0113 g. of sodium in 5·590 g. of ammonia. At the minimum, which occurred when about 70% of stannane needed to form stannylsodium had been added, the blue colour of the solution had just disappeared. Since the minimum occurred at a lower hydride : sodium ratio than unity, we concluded that at this stage some of the sodium was present as stannylenedisodium, SnH_2Na_2, which later reacted with fresh stannane to form stannylsodium. When enough stannane had been added to give a ratio of reactants of just above unity the conductivity became constant and only stannylsodium was present. This was borne out by measurement of the hydrogen evolved in the thermal decomposition of the end product after the removal of ammonia. It corresponded in amount with the decomposition of H_3SnNa. The initial

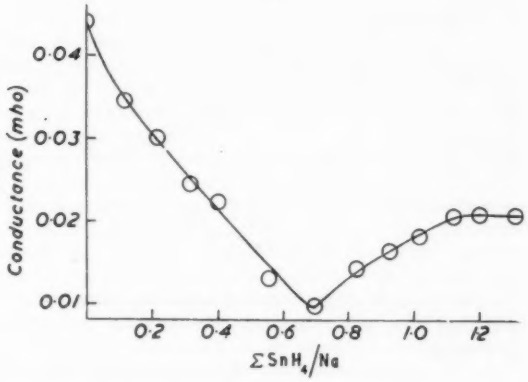

FIG. 1. *Conductometric titration of a solution of sodium in liquid ammonia with gaseous stannane.*

sodium solution had an equivalent conductivity of 786 ohm^{-1} $cm.^{-1}$, and the stannylsodium solution had the high value of 372 ohm^{-1} $cm.^{-1}$.

The hydrogen evolution as a function of the mole-fraction of stannane added is shown in Fig. 2. The ratio of total hydrogen evolved to total stannane added (ordinate) would have a value of 1·0 for the formation of H_2SnNa_2 and of 0·5 for H_3SnNa. The curve is consistent with the initial formation of the former, and its gradual transformation into the latter. The final value for the hydrogen evolution is 0·55 and not 0·5 owing to a little decomposition of stannane to tin and hydrogen in the later stages of the titration, when no free sodium was present. The tin was deposited as a mirror above the level of the ammonia solution. The direct formation of sodamide from sodium and ammonia is unlikely since both stannylsodium and stannylenedisodium can be formed quantitatively under suitable conditions and characterised by the hydrogen evolved in their decompositions. It was shown in preliminary experiments that the reaction $H_3SnNa + Na = H_2SnNa_2 + \frac{1}{2}H_2$ occurs very slowly at −63·5°, as does the corresponding reaction of germanylsodium. Even after 10 hr. the conversion of 0·0876 g. of stannylsodium into stannylenedisodium by a two-fold excess of sodium was only 30% complete.

Stannylenedisodium was prepared by reaction of a tenfold excess of sodium with stannane in ammonia at −63·5°. Excess of sodium was removed by reaction with ethyl chloride, which did not react with stannylenedisodium. Decomposition of the ammonia-free compound was not appreciable until 0° but at 15° was complete in half an hour, hydrogen evolution being in accord with the equation $H_2SnNa_2 = SnNa_2 + H_2$. After removal of sodium, stannylenedisodium did not react with methyl iodide in ammonia

and the hydrogen evolved in its subsequent decomposition at room temperature after removal of ammonia was equimolar with the amount of stannane used in the preparation. Stannylsodium was less stable and decomposed at −63·5° as soon as ammonia was removed. The hydrogen evolved was in accord with the equation $H_3SnNa = SnNa + \frac{3}{2}H_2$. It is probable that stannylsodium, like germanylsodium,[3] is stable only as an ammine.

Stannylsodium reacted with alkyl iodides at −63·5° in ammonia solution to form alkylstannanes and sodium iodide. Methyl-, ethyl-, and *n*-propyl-stannanes were so prepared. Their stability decreased with increase in the molecular weight of the organic radical and, in the case of the *n*-propyl derivative, was so low at room temperature that the yield was poor. This type of reaction is also found for germanylsodium.[4] Stannylsodium, like germanylsodium, did not react with methylene chloride.

Organostannanes were first made by the action of an ammonium halide in liquid ammonia on the appropriate organostannylsodium. In this way, trimethyl-, triphenyl-, and diphenyl-stannane were prepared.[5] Monogermane can also be similarly regenerated

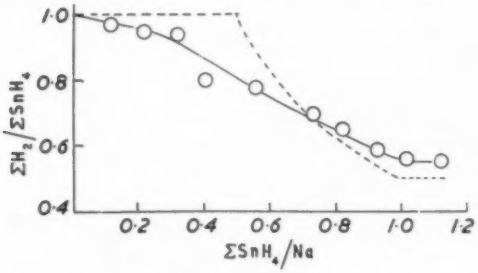

FIG. 2. *Hydrogen evolution during the titration of a solution of sodium in liquid ammonia with gaseous stannane.*

The broken line shows the hydrogen evolution expected if stannylenedisodium had been first formed and later converted into stannylsodium.

from germanylsodium[3] and it has been shown that both stannylsodium and stannylenedisodium also react in this way with a solution of ammonium chloride in ammonia at −63·5°:

$$H_3SnNa + NH_4Cl = SnH_4 + NaCl + NH_3$$

$$H_2SnNa_2 + 2NH_4Cl = SnH_4 + 2NaCl + 2NH_3$$

The high yield of stannane obtained in the reduction of stannic chloride by lithium aluminium hydride (80—90% based on $LiAlH_4$, according to $SnCl_4 + 4LiAlH_4 = SnH_4 + 4LiCl + 4AlH_3$) suggested that plumbane, PbH_4, might be similarly obtained from plumbic chloride. At −78° plumbic chloride and lithium aluminium hydride reacted in ether to give metallic lead.

Three claims to the preparation of plumbane have been made,[7] although all have been criticised.[8] Piper and Wilson failed to prepare plumbane by the reduction of plumbous chloride with sodium borohydride, although this method gives good yields of germane[9] and stannane.[10] Plumbane probably does not exist as a stable compound, although it may be formed as a reaction intermediate, *e.g.*, in the reduction of plumbic chloride by lithium aluminium hydride.

EXPERIMENTAL

Stannane was prepared by a modification of Finholt and Schlesinger's method.[6] An ether slurry of the solid ether adduct of stannic chloride was put in the reaction vessel and frozen

[4] Teal and Kraus, *J. Amer. Chem. Soc.*, 1950, **72**, 4706; Kraus and Carney, *ibid.*, 1934, **56**, 765.
[5] Kraus and Greer, *ibid.*, 1922, **44**, 2629; Chambers and Scherer, *ibid.*, 1926, **48**, 1054.
[6] Finholt, Schlesinger, Wilzbach, and Bond, *ibid.*, 1947, **69**, 2692.
[7] Paneth and Nörring, *Ber.*, 1920, **53**, 1693; Schultze and Müller, *Z. phys. Chem.*, 1930, *B*, **6**, 267; Weeks, *J.*, 1925, **127**, 2845.
[8] See, for example, Pearson, Robinson, and Stoddart, *Proc. Roy. Soc.*, 1933, *A*, **142**, 275; Hurd, "Chemistry of the Hydrides," 1952, p. 118.
[9] Piper and Wilson, *J. Inorg. Nuclear Chem.*, 1957, **4**, 22.
[10] Schaeffer and Emilius, *J. Amer. Chem. Soc.*, 1954, **76**, 1203.

in liquid nitrogen. An ether solution of lithium aluminium hydride was added and frozen. A stream of nitrogen containing 0·1% of oxygen to inhibit the decomposition of the stannane was passed and the reaction vessel was warmed to −78° until the ether was liquid and then to −63·5° until the solution was brown. The temperature was allowed to increase gradually (1 hr.) to −20°, and evolution of stannane was then complete. The gas was collected in a trap cooled in liquid nitrogen and purified by repeated passage through a trap cooled to −112°, which condensed traces of ether and allowed stannane to pass. Purity was checked by molecular-weight and vapour-pressure measurements. The stannane was stored as gas at room temperature with about 10% of oxygen from which it was freed as required by condensation. In a typical run 22·3 g. of ether adduct and 10 g. of lithium aluminium hydride gave 6·7 g. of pure stannane.

The conductivity cell was cylindrical (1·7 cm. diam., 20 cm. long), with two blackened platinum electrodes, each of 1 cm.^{2} area, held in long glass leads. The cell constant was 1·75. It was connected by a tap and standard joint to a vacuum fractionation apparatus. The solution of sodium in liquid ammonia was prepared by rapidly weighing a piece of freshly-cut reagent grade sodium (*ca.* 0·01 g.), putting it in the cell and evacuating. Ammonia (*ca.* 2 ml.), dried over sodium, was condensed into the cell and kept for 30 min. at −63·5° to obtain a homogeneous solution. No hydrogen was evolved. The conductivity was measured at −63·5°. About one-tenth of the stannane required to give a SnH_4 : Na ratio of unity was weighed as gas and condensed into the cell by cooling it in liquid nitrogen. It was allowed to react with sodium at −63·5° for 15 min., and the conductivity and hydrogen evolved were then measured. This was repeated after successive additions of stannane up to a 1 : 1 ratio. At the end of the run the ammonia was removed and weighed.

Preparation and Properties of Stannylsodium.—Sodium (0·0145 g.) was dissolved in ammonia (~3 g.) in a reaction tube attached to the vacuum apparatus. The solution was frozen in liquid nitrogen and stannane (0·0824 g.) condensed in. After ½ hr. at −63·5° hydrogen was pumped off and measured by volume (Found: H, 0·000654 g. Calc. for reaction to form H_3SnNa: H, 0·000634 g.). Ammonia was pumped off at −63·5°. As the last of the solvent was removed the solution became black and hydrogen was evolved slowly. Decomposition was rapid at 0°. The total hydrogen was measured (Found: H, 0·00196 g. Calc. for decomposition of 0·0916 g. of H_3SnNa: H, 0·00192 g.). The black solid residue gave hydrogen and an alkaline solution on addition of water, forming a black solid which gave the *X*-ray pattern of white tin. In a second experiment decomposition of stannylsodium was rapid at 0°, even in presence of a 40 cm. pressure of ammonia. There was no evidence that an ammine was formed.

Reactions of Stannylsodium.—(a) *With methyl iodide.* Methyl iodide (0·1 g.) was condensed on a frozen solution of stannylsodium (0·117 g.) in ammonia, prepared as above. There was an immediate white precipitate on warming to −63·5°. After 5 min. volatile products were washed with a solution of copper sulphate in 10% sulphuric acid to remove ammonia. The decomposition of the methylstannane, which would otherwise have been catalysed by the ammonia, was inhibited by the oxygen dissolved in the solution. The residual volatile material was dried by passage through a trap at −95°. The product was methylstannane (0·100 g.; yield 94% on stannane taken), b. p. 1·4° (extrapolated) (lit.,[6] 0°) (Found: *M*, 137. Calc. for CH_6Sn: *M*, 137). The infrared spectrum was identical with that of a specimen made by reducing methyltrichlorostannane with lithium aluminium hydride, having the following peaks: 3692 (w), 3000 (m), 2932 (m), 2835 (w), 1875 (v.s.) broad, 1751 (w), 1583 (w), 1464 (w), 1265 (w), 1145 (w), 700 (s), 680 cm.$^{-1}$ (s).

(b) *With ethyl iodide.* The above procedure was used (stannylsodium, 0·101 g.; ethyl iodide, 0·08 g.). The product, dried by passage as vapour through a trap at −78°, was *ethylstannane* (0·036 g.), b. p. 25° (extrapolated) (Found: *M*, 151. C_2H_8Sn requires *M*, 151). The infrared spectrum showed the following peaks: 2940 (m), 1869 (v.s.), 1470 (w), 1382 (w), 1208 (w), 1195 (w), 1020 (w), 686 (v.s.), 674 cm.$^{-1}$ (s). The compound decomposed slowly at room temperature.

(c) *With* n-*propyl iodide.* Using the same procedure (stannylsodium, 0·0982 g.; *n*-propyl iodide, 0·07 g.), and removing water at −63·5°, we obtained n-*propylstannane* (0·0458 g.) (Found: *M*, 165. $C_3H_{10}Sn$ requires *M*, 165). It decomposed before either its infrared spectrum or vapour-pressure curve could be obtained.

(d) *With ammonium chloride.* Ammonium chloride (~2·5 g.) was added slowly by a rotating

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arm to a solution of stannylsodium (0·111 g.) in liquid ammonia at −63·5°. Stannane (0·0613 g., 80%) was evolved (Found: *M*, 122. Calc. for H_4Sn: *M*, 123) and separated from ammonia as described above. The infrared spectrum was identical with that of stannane.

Preparation and Properties of Stannylenedisodium.—The same method was used as for stannylsodium with stannane (0·0530 g.) and a ten-fold excess of sodium (0·12 g.). The hydrogen evolved was 0·001064 g. (Calc. for complete conversion into H_2SnNa_2: 0·001060 g.). When only a two-fold excess of sodium was used the hydrogen evolved corresponded with a mixture of H_3SnNa (~10%) and H_2SnNa_2 (~90%). Excess of sodium was removed by adding ethyl chloride (0·5 g.) to the frozen ammonia solution of stannylsodium, allowing it to react at −63·5° (10 min.) and pumping off excess of ethyl chloride and solvent ammonia at −63·5°. Fresh ammonia was then condensed into the reaction vessel.

Stannylenedisodium did not decompose when ammonia was removed at −63·5°. When the temperature was raised gradually (5 hr.) to −20°, hydrogen evolution showed 3% decomposition. Decomposition was complete in 30 min. at 15°, 0·0883 g. (0·000530 mole) of H_2SnNa_2 giving 0·00105 g. (0·000525 mole) of hydrogen. The black decomposition residue reacted with water with a yellow flash, hydrogen evolution and formation of a residue with the *X*-ray pattern of white tin.

Reactions of Stannylenedisodium.—(a) *With ethyl chloride and methyl iodide.* Excess of ethyl chloride (1·0 g.) was added to a solution of stannylenedisodium (0·204 g.) in liquid ammonia from which excess of sodium had not been removed. There was immediate reaction at −63·5° between sodium and ethyl chloride. After ½ hr. ammonia was removed chemically as before and the volatile residue passed through a trap at −95° to condense diethylstannane and water. The condensate showed no trace in its infrared spectrum of the very strong Sn–H stretching frequency at 1875 cm.$^{-1}$. The residue in the reaction vessel decomposed on warming and evolved 0·0244 g. of hydrogen (Calc. for 0·204 g. of H_2SnNa_2: 0·0245 g.). With stannylenedisodium (0·133 g.) from which excess of sodium had been removed with ethyl chloride, there was no evidence for the formation of a methylstannane on treatment as before with methyl iodide (0·217 g.). After removal of all volatile products thermal decomposition of the residue gave 0·00186 g. of hydrogen (Calc. for 0·133 g. of H_2SnNa_2: 0·00184 g.).

(b) *With ammonium chloride.* Stannylenedisodium (0·169 g.) with ammonium chloride (~2·5 g.) in ammonia solution gave 0·0812 g. of stannane (theoretical 0·124 g.). The infrared spectrum was identical with that of stannane.

Attempted Preparation of Plumbane.—An attempt was made to prepare plumbane by the reduction of plumbic chloride with lithium aluminium hydride. The apparatus was that used for the preparation of stannane. The ether adduct of 10 g. of plumbic chloride was made and quickly frozen in the reaction vessel. After addition and freezing of a mixture of ether and solid lithium aluminium hydride (8 g.) the reaction vessel was warmed, first to −96° and then, when the ether had liquefied, to −78°. At this temperature the plumbic chloride was slowly reduced to a black powder which *X*-ray powder photography showed to be metallic lead. Throughout the preparation nitrogen was bubbled through the solution, the volatile products being collected in liquid-nitrogen traps. At the end of the reaction the material in these traps was found to be completely condensed in a trap cooled to −95°. The condensate was ether [Found: *M*, 73·5. Calc. for $(C_2H_5)_2O$: *M*, 74·0], its infrared spectrum had no adsorption in addition to that expected for ether, and no metallic mirror was formed on standing at room temperature.

One of us (S. F. A. K.) thanks the Department of Scientific and Industrial Research for a Maintenance Grant.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, January* 17*th*, 1958.]

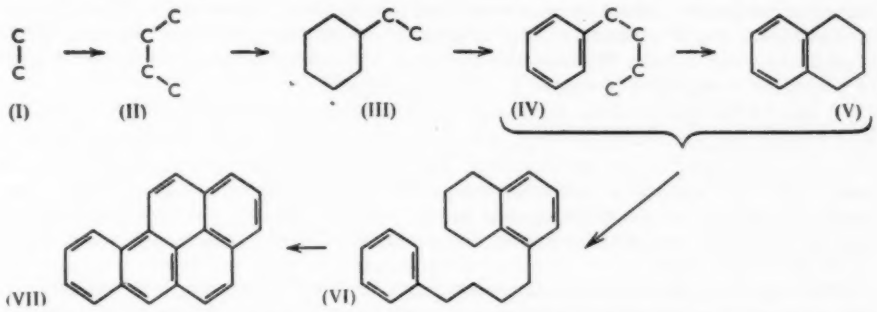
498. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part I. Introduction.*

By G. M. Badger, R. G. Buttery, R. W. L. Kimber, G. E. Lewis, A. G. Moritz, and I. M. Napier.

A mechanism for the formation of 3 : 4-benzopyrene from simple components is considered. The techniques used to separate and identify components of complex hydrocarbon tars are reported.

When 3 : 4-benzopyrene was first isolated from coal tar [1] it was recognised as the probable cause of certain "industrial" cancers. In recent years, however, 3 : 4-benzopyrene and other polycyclic aromatic hydrocarbons have been identified in a great variety of materials; [2-12] this widespread occurrence has obvious implications in connection with the incidence of cancer among the general population, and it is important to determine the origin and mode of the formation of such carcinogenic hydrocarbons.

The carcinogenic hydrocarbons which occur in human environment seem to be formed only at high temperature. The "primary" tar produced by heating coal at 300—450° in absence of air consists mainly of paraffins, *cyclo*paraffins, olefins, and phenols. At higher temperatures this mixture undergoes various transformations to give a "secondary" tar containing a greater proportion of polycyclic aromatic compounds. Kennaway [13] found that although tar produced from a Durham Holmside coal at 450°



had slight carcinogenic activity, tars produced at 560° and at 1250° were much more potent. Similarly, certain petroleums became carcinogenic after being heated,[13] and Scottish shale oil was carcinogenic only after pyrolysis.[14] Carcinogenic tars and tars containing polycyclic aromatic hydrocarbons have been produced by pyrolysis of

[1] Cook, Hewett, and Hieger, *J.*, 1933, 395.
[2] Goulden and Tipler, *Brit. J. Cancer*, 1949, **3**, 157; Passey, *Brit. Med. J.*, 1922, ii, 1112.
[3] Sulman and Sulman, *Cancer Res.*, 1946, **6**, 366; Beránková and Sůla, *Časopis Lékařů, Českýeh*, 1953, **92**, 195; *Chem. Abs.*, 1955, **49**, 592.
[4] Cooper, *Chem. and Ind.*, 1953, 1364; Cooper and Lindsey, *ibid.*, 1953, 1177; 1260; Clemo, *ibid.*, 1953, 557; 1955, 38; Waller, *Brit. J. Cancer*, 1952, **6**, 8; Leiter, Shimkin, and Shear, *J. Nat. Cancer Inst.*, 1942, **3**, 155; Shore and Katz, *Analyt. Chem.*, 1956, **28**, 1399.
[5] Falk, Steiner, Goldfein, Breslow, and Hykes, *Cancer Res.*, 1951, **11**, 318.
[6] Falk and Steiner, *ibid.*, 1952, **12**, 30; von Haam and Mallette, *Arch. Industr. Hyg.*, 1952, **6**, 237.
[7] Kotin, *Cancer Res.*, 1956, **16**, 375.
[8] Gilbert and Lindsey, *Chem. and Ind.*, 1956, 927.
[9] Hougen, *ibid.*, 1954, 192.
[10] Campbell and Lindsey, *Chem. and Ind.*, 1955, 64; 1957, 951.
[11] *Idem, Brit. J. Cancer*, 1956, **10**, 649.
[12] Cooper, Lindsey, and Waller, *Chem. and Ind.*, 1953, 1205; 1954, 1418; Gilbert and Lindsey, *Brit. J. Cancer*, 1956, **10**, 642; Bonnet and Neukomm, *Helv. Chim. Acta*, 1956, **39**, 1724; Patton and Touey, *Analyt. Chem.*, 1956, **28**, 1685; Philippe and Hobbs, *ibid.*, 1956, **28**, 2002; Gilbert and Lindsey, *Brit. J. Cancer*, 1956, **10**, 646.
[13] Kennaway, *Brit. Med. J.*, 1925, ii, 1.
[14] Berenblum and Schoental, *Brit. J. exp. Path.*, 1943, **24**, 232.

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cholesterol,[15] skin,[13] yeast,[13] isoprene,[13,16] acetylene,[13] diacetyl,[17] and aliphatic hydrocarbons from tobacco.[18]

The formation of aromatic hydrocarbons from aliphatic compounds at high temperatures has not been extensively studied. It seems, however, that the most important reactions are cracking, diene syntheses, dehydrogenations, and cyclodehydrogenations. Polycyclic compounds may be formed by a series of such reactions, and the present work was designed to study the formation of 3 : 4-benzopyrene (VII) and related carcinogenic hydrocarbons at high temperatures. As a working hypothesis it has been assumed that 3 : 4-benzopyrene may be formed by the series of reactions (I→VII). This presupposes that benzopyrene will be formed by pyrolysis of any of the intermediate compounds, and has governed the initial choice of materials to be pyrolysed. The state of hydrogenation of the intermediate compounds would seem to be unimportant as hydrogenations and dehydrogenations occur easily at high temperatures.

The available experimental evidence, which is meagre, supports the view that benzopyrene is formed from simpler units by a stepwise synthesis. Pyrolysis of acetylene (I) is known to give aromatic hydrocarbons,[19] and the crude tar is carcinogenic.[13] Its fluorescence spectrum is diffuse but not inconsistent with the presence of 3 : 4-benzopyrene.[20] In this connection, incomplete combustion of organic compounds often gives acetylene,[21] and acetylene has been detected in tobacco smoke.[22] A four-carbon unit (II), such as vinylacetylene or butadiene, seems the most logical intermediate in the formation of the " tars," and small quantities of the former have been reported among the products.[22] Butadiene undergoes diene synthesis with itself to give vinyl*cyclo*hexene, and the pyrolysis of butadiene yields relatively large amounts of ethylbenzene and styrene (III).[23] Naphthalene and tetralin (V) were also formed in this pyrolysis and the complex mixture of polycyclic compounds contained 3 : 4-benzopyrene.[23]

A clue to the nature of the final steps of the synthesis is provided by the observation that tetralin and aluminium chloride give a complex mixture which becomes carcinogenic after being heated.[24] This carcinogenic tar has a diffuse fluorescence spectrum in the same region as that of 3 : 4-benzopyrene. 6-4′-Phenylbutyltetralin is known to be a major constituent of the mixture, and it has been suggested[25] that some 5-4′-phenylbutyltetralin (VI) may also be formed and pass, rather easily, into 3 : 4-benzopyrene by cyclodehydrogenation.

Although this mechanism has been used as a working hypothesis, it is unlikely that any polycyclic compound will be formed by any single scheme. Moreover, the supposed intermediates may be produced from fragments larger than acetylene, and complex hydrocarbons need not necessarily break down to two-carbon fragments before re-synthesis. The C_6–C_4 fragments (IV and V), for example, could arise by cyclisation of a C_{10} hydrocarbon such as *n*-decane.[26] or from a higher hydrocarbon (such as dicetyl) by cracking followed by cyclisation.

The experimental section describes some general methods and techniques used in the investigations.

[15] Kennaway and Sampson, *J. Path. Bact.*, 1928, **31**, 609; Falk, Goldfein, and Steiner, *Cancer Res.*, 1949, **9**, 438.
[16] Kennaway, *J. Path. Bact.*, 1924, **27**, 233.
[17] Lam, *Acta Path. Microbiol. Scand.*, 1956, **39**, 198.
[18] *Idem*, *ibid.*, 1955, **37**, 421; 1956, **39**, 207.
[19] Berthelot, *Ann. Chim.*, 1866, **9**, 445; Zelinsky, *Compt. rend.*, 1923, **177**, 882; *Ber.*, 1924, **57**, 264.
[20] Kennaway, *Biochem. J.*, 1930, **24**, 497.
[21] Nieuwland and Vogt, " The Chemistry of Acetylene," Reinhold, New York, 1945.
[22] Fishel and Haskins, *Ind. Eng. Chem.*, 1949, **41**, 1374.
[23] Weizmann *et al.*, *ibid.*, 1951, **43**, 2312, 2318, 2322, 2325.
[24] Schroeter, *Ber.*, 1924, **57**, 1990; Kennaway, *Biochem. J.*, 1930, **24**, 497; Hieger, *ibid.*, 1930, **24**, 505.
[25] Cook and Hewett, *J.*, 1933, 398; cf. Grove, *J.*, 1953, 483.
[26] Rozenberg, *Doklady Akad. Nauk S.S.S.R.*, 1950, **73**, 719; see also, Hansch, *Chem. Rev.*, 1953, **53**, 353.

Experimental

Furnace.—This consisted of a silica tube (3 ft. × 1 in. i.d.) wound along its length with 25 s.w.g. Nichrome wire (total resistance 90 ohms). A calibrated chromel–alumel thermocouple was inserted through a small hole bored near the centre of the tube. The tube was mounted along the centre of a pressed asbestos-board box (3 × 1 × 1 ft.) filled with " vermiculite." The material to be pyrolysed was passed through a second silica tube (3 ft. 6 in. × ¾ in. i.d.) which just fitted into the heated tube. The furnace was inclined at 10° to the horizontal to facilitate collection of products.

Chromatography on Alumina.—Hexane or benzene was generally used as solvent and/or eluant. Thiophen-free benzene was washed with concentrated sulphuric acid and then water, and distilled. Hexane was also washed with concentrated sulphuric acid, then water, and fractionally distilled.

Gas–Liquid Partition Chromatography.—This was of great value in analyses of mixtures formed by pyrolysis of acetylene, styrene, etc. A Pyrex column (3 ft. × 6 mm. i.d.) was packed with alkali- and acid-washed Celite 545 (30—60 mesh) coated with Apiezon L high-vacuum grease (4 g./8 g. of Celite). The column and detecting and reference cells were mounted in a box (3 ft. × 1 ft. × 6 in.) of asbestos board, lined with aluminium foil. Heating was provided by three 1-kw radiator bars mounted in the box at one end, air being circulated by a powerful fan. Baffles increased circulation and prevented heating by radiation. The detecting and reference cells were A2321/100 thermistors,[27] sealed in T-tube Pyrex cells and enclosed in a brass " heat sink." The electrical detecting circuit was of normal bridge type [28] with the detecting and reference thermistors in the two arms of the bridge and 100-ohm fixed resistors in the other arms. A bridge voltage of 4—8 volts was used. Nitrogen was used as carrier gas, and the sample was injected by hypodermic syringe through a rubber cap. Solid samples were injected as solutions in xylene, mesitylene, or tetralin.

Each fraction was collected as it left the column. For the lower-boiling products a V-tube collector was connected *via* a B10 joint to the end of the detecting cell through a hole cut in the hot-air bath, the end of the V being cooled. For higher-boiling products a straight tube, with air cooling, was used. Polycyclic compounds were separated by chromatography under vacuum, a two-tube collector (two parallel tubes sealed to a B10 joint), with air cooling, being used. The dimensions of the collector were such that, when connected to the collector cell, the seal was well inside the hot-air bath. Under normal conditions the gas passed through one tube and only when a particular fraction was to be collected was the gas flow switched to the other; for this purpose a two-way tap was connected to the two tubes by pressure tubing.

Identification of Products.—Fractions from gas–liquid chromatograms were provisionally identified by comparison of retention times or of the ratio of their retention times to those of known substances under the same conditions. The identification was confirmed by collecting the fraction and determining the infrared, ultraviolet, or fluorescence spectrum or, in appropriate cases, by mixed m. p. determination and the preparation of derivatives. Fractions separated by fractional distillation and chromatography on alumina were similarly identified.

Infrared Spectra.—These were determined with a Grubb-Parsons double-beam instrument. Solids were examined as solutions in carbon tetrachloride. The spectra were compared with published curves, or with curves obtained from authentic specimens.

Fluorescence Spectra.—A direct-vision hand spectroscope (R. & J. Beck, Ltd.) calibrated from 400 to 700 mμ in 10 mμ divisions was used. A prism was fitted to cover half the slit so that unknown and standard solutions could be examined simultaneously. Provision was made for momentary illumination of the scale by a bezzle lamp, the light being diffused by frosted-glass plates. A 35-mm. camera, with a 50-mm. focal-length lens, and fitted with a 2 dioptre supplementary lens, was mounted directly in front of the eyepiece. The whole apparatus, except the camera, was enclosed in a light-tight box. The excitation radiation was from an enclosed 125 w mercury lamp, fitted to the outside of the box. Visible light was almost completely removed by passage through Wood's glass windows, leaving mainly the 3650 Å mercury line. The instrument was calibrated against mercury, neon, hydrogen, and sodium lines. In the 400 mμ region the expected accuracy is within 1 mμ, and in the 500 mμ region, within 5 mμ. Standard solutions were in the following concentrations: 3 : 4-benzopyrene, 5×10^{-4} mole/l.,

[27] Ambrose and Collerson, *J. Sci. Instr.*, 1955, **32**, 323.
[28] Dibat, Porter, and Stross, *Analyt. Chem.*, 1956, **28**, 290.

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anthracene, 10^{-3} mole/l., and 1 : 2-benzanthracene, 5×10^{-4} mole/l. The solvent was usually benzene; but unknown products were always examined in the same solvent as the standard materials. With solutions of the above concentration a spectrometer slit-width of 0·01 in., and an exposure time of 1 min. at *f*2·9 with Kodak Tri-X film were usually satisfactory. The scale was illuminated for 0·2—0·5 sec. With this apparatus, 3 : 4-benzopyrene (5×10^{-4} mole/l. in benzene) gave a fluorescence spectrum showing considerable fine structure (Table 1).

TABLE 1. *Maxima* (mμ) *of fluorescence bands for* 3 : 4-*benzopyrene.*

Weigert [a] (acetone)	Chalmers [b] (alcohol)	Schoental [c] (light petroleum)	Cardon [d] (benzene)	Present work (benzene)
—	394	—	—	398 weak, B *
404	404·5	403	—	404 strong, N
410	410	408	410	409 weak, N
417	417	415	413	417 weak, N
427	429	427	—	427 strong, B
—	434	431	432	433 strong, B
—	—	437	—	437 v. weak, N
455	456	454	455	456 strong, B
485	—	—	—	485 weak, B

* B = Broad band; N = Narrow band.

[a] Weigert and Mottram, *Nature*, 1940, **145**, 895. [b] Chalmers, *Biochem. J.*, 1938, **32**, 271. Schoental and Scott, *J.*, 1949, 1683. [d] Cardon, Alvord, Rand, and Hitchcock, *Brit. J. Cancer*, 1956, **10**, 485.

TABLE 2. *Maxima* (mμ) *of fluorescence bands for perylene.*

Radulescu [a] (benzene)	Radulescu [a] (heptane)	Schoental [b] (light petroleum)	Present work (benzene)
446	440	438	445 B
475	465	465	475 B
505	498	497	502 B
537·5	535	—	536 B

[a] Radulescu and Dragulescu, *Bul. Soc. chim. România*, 1935, **17**, 9, 26, 35. [b] Schoental and Scott, *loc. cit.*

With weaker or impure solutions only the strong bands were normally detected. Perylene showed maxima as recorded in Table 2.

Ultraviolet Spectra.—Most of these were measured in 95% ethanol on a Hilger Uvispek spectrophotometer.

The work described in Parts I—IV has been supported by the Damon Runyon Memorial Fund (R. G. B. and R. W. L. K.); we are also indebted to the University of Adelaide Anti-Cancer Campaign for a maintenance grant (I. M. N.). One of us (A. G. M.) has a C.S.I.R.O. scholarship. The infrared spectrometer was purchased with a grant from the Rockefeller Foundation. Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory, Melbourne.

UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA. [*Received, January* 24*th*, 1958.]

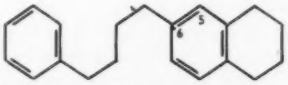
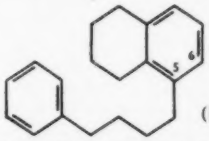
499. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part II.* An Examination of "Schroeter Tar."*

By G. M. Badger and R. W. L. Kimber.

3 : 4-Benzopyrene has been isolated from "Schroeter tar," formed by the action of aluminium chloride on tetralin.

When tetralin is treated with aluminium chloride a complex mixture ("Schroeter tar") is obtained,[1] which is carcinogenic after being heated.[2] The fluorescence spectrum of this mixture is similar to that given by other carcinogenic tars,[3] and the presence of 3 : 4-benzopyrene has long been presumed. Schroeter[1] showed that the mixture contained 6-4′-phenylbutyltetralin (I), and Cook and Hewett[4] suggested that it may also contain 5-4′-phenylbutyltetralin (II). This could give 3 : 4-benzopyrene by cyclodehydrogenation; it is a very likely intermediate, and may be difficult to detect owing to its rapid conversion.

"Schroeter tar" has now been distilled; several fractions gave diffuse fluorescence spectra corresponding to 3 : 4-benzopyrene. By chromatography on alumina, 3 : 4-benzopyrene has been isolated and characterised. A fraction, b. p. 205—240°/0·5 mm., which approximately corresponds to that which Kennaway[2] found to be strongly carcinogenic, contains as much as 4% of 3 : 4-benzopyrene. No 1 : 2-benzopyrene could be detected, but there was some evidence for the presence of perylene. Another hydrocarbon was isolated from the fraction of highest boiling point, but has not been identified.

(I)   (II)

5-4′-Phenylbutyltetralin (II) could not be detected, although the 6-isomer and 2 : 6′-ditetralyl were isolated in agreement with Schroeter.[1] Oxidation of the appropriate fraction with potassium permanganate[1] and esterification of the resulting acid with diazomethane gave trimethyl benzene-1 : 2 : 4-tricarboxylate but none of the 1 : 2 : 3-isomer [which would be formed by oxidation of (II)].

These experiments did not eliminate the possibility that 5-4′-phenylbutyltetralin (II) might be present in small amounts; but if so it should be cyclodehydrogenated to 3 : 4-benzopyrene when heated further. The fraction, b. p. 230—240°/15 mm., from which virtually all the 3 : 4-benzopyrene had been removed was accordingly pyrolysed at 360° and at 600°. Only a trace of 3 : 4-benzopyrene could be detected after heating at the lower temperature. Heating at 600° resulted in considerable decomposition and gave a complex tar in which naphthalene, 2-methylnaphthalene, and 2-ethylnaphthalene were positively identified. Peaks corresponding to toluene, ethylbenzene, styrene, and other simple products were observed in the gas-phase chromatogram. A hydrocarbon having a phenanthrene-type spectrum was isolated and 2 : 2′-dinaphthyl was also formed in reasonable quantity. Traces only of perylene and 3 : 4-benzopyrene were detected.

Experimental

"Schroeter Tar."—A mixture of tetralin (2·5 kg.) and aluminium chloride (50 g.) was stirred for 10 hr. at 50—70°, then poured on ice. The product was collected and distilled. After removal of the lower-boiling fraction (containing benzene, tetralin, octahydroanthracene, and octahydrophenanthrene [1]), three fractions were collected: (i) b. p. 230—240°/15 mm. (280 g.);

* Part I, preceding paper.

[1] Schroeter, *Ber.*, 1924, **57**, 1990.
[2] Kennaway, *Biochem. J.*, 1930, **24**, 497.
[3] Hieger, *ibid.*, p. 505.
[4] Cook and Hewett, *J.*, 1933, 398.

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(ii) b. p. 205—240°/0·5 mm. (75 g.); and (iii) b. p. 245—300°/1 mm. (71 g.). All fractions having b. p. greater than 120°/15 mm. showed fluorescence bands corresponding to 3 : 4-benzopyrene.

Analysis of Fraction (*i*).—The crude fraction (63 g.) was chromatographed in hexane on alumina. The main bulk was eluted with hexane (1 l.), but further elution with benzene–hexane (1 : 2) gave 8 fractions (of 70 c.c.) showing strong 3 : 4-benzopyrene fluorescence spectra. Evaporation of the solvent and recrystallisation of the solid (60 mg.) from ethanol gave 3 : 4-benzopyrene, m. p. and mixed m. p. 174—176° (lit. 176—177°); $\lambda_{max.}$ (log ε) (in ethanol) 226 (4·40), 255 (4·58), 265 (4·65), 274 (4·44), 284 (4·62), 296 (4·73), 331 (3·65), 347 (4·04), 364 (4·30), 384 (4·37), 404 (3·50) in good agreement with the literature.[5] The spectrum also showed a maximum at 434 mμ (2·78) presumably due to contamination (<1%) with perylene (lit.,[6] 434 mμ).

Analysis of Fraction (*ii*).—The crude fraction (55 g.) was chromatographed as for fraction (i). Elution with benzene–hexane gave 8 fractions (of 175 c.c.), but most of the 3 : 4-benzopyrene was present in fractions 2—5.

Evaporation of the solvent gave crude 3 : 4-benzopyrene (2·1 g.). After recrystallisation this had m. p. and mixed m. p. 174—175° (Found: C, 95·0; H, 5·0. Calc. for $C_{20}H_{12}$: C, 95·2; H, 4·8%). The trinitrobenzene complex had m. p. 223—224° [lit., 226—227° (corr.)] (Found: C, 67·15; H, 3·2. Calc. for $C_{26}H_{15}O_6N_3$: C, 67·1; H, 3·2%). Absorption spectroscopy showed perylene to be present (<1%).

Analysis of Fraction (*iii*).—This fraction (71 g.) was chromatographed as above. The fractions eluted with benzene–hexane were combined (1·5 l.) and evaporated. The residue, in benzene, was then extracted with cold concentrated sulphuric acid, the acid solution poured on ice, the mixture extracted with benzene, and the benzene solution washed and dried. Further chromatography and elution with benzene–hexane gave an orange residue (20 mg.) which formed orange-brown prisms, m. p. 255—257°; $\lambda_{max.}$ 220, 246, 255, 269, 297, 310, 323, 354, 374, 396, 422, 448, and 456 (infl.) mμ.

Pyrolysis at 360°.—Fraction (i) (2 g.) from which the 3 : 4-benzopyrene had been removed by chromatography was refluxed for 1 hr. Chromatography of the product on alumina yielded traces (*ca.* 0·5 mg.) of 3 : 4-benzopyrene and perylene as estimated from the ultraviolet spectra.

Pyrolysis at 600°.—Fraction (i) (20 g.) from which the benzopyrene had been removed was vapourised at the rate of 1 drop/15 sec. and passed with nitrogen (1 c.c./sec.) through a silica tube (36 in. × 1 in.) packed with porcelain chips (3/8 in.—1/4 in.) heated to 600°. Distillation of the resulting tar gave fractions: F1, b. p. 80° (0·25 g.); F2, b. p. 80—120° (0·5 g.); F3, b. p. 80—110°/21 mm. (3 g.); F4, b. p. 110—120°/21 mm. (2·5 g.); F5, b. p. 120—140°/21 mm. (0·5 g.); F6, b. p. 100—150°/1·2 mm. (3 g.); F7, b. p. 150—180°/1·2 mm. (2 g.); F8, b. p. 180—220°/1·2 mm. (1 g.); and the residue (2 g.).

Gas-phase chromatography of fractions F1—3 gave peaks with retention times corresponding to toluene, ethylbenzene, styrene, three unknown substances, naphthalene, and 2-methylnaphthalene. Naphthalene was collected from the chromatogram and identified by m. p. and mixed m. p. 2-Methylnaphthalene was collected; its infrared spectrum showed maxima at 5·18, 5·38, 5·53, 5·66, 6·08, 6·23, 6·98, 7·12, 7·28, 7·36, 7·55, 7·89, 8·10, 8·32, 8·53, 8·67, 8·76, 8·89, 9·64, 10·44, and 14·34 μ in substantial agreement with the literature.[7] It also showed maxima at 5·90, 6·85, 7·22, 7·42, and 9·28 μ probably indicative of 1-methylnaphthalene.

Fractions F4—5 showed the presence of naphthalene, 1-methylnaphthalene, and 2-ethylnaphthalene. The latter was collected, and showed maxima in the infrared region at 5·20, 5·42, 5·61, 5·85, 6·10, 6·23, 7·88, 8·30, 8·55, 8·67, 8·76, 8·89, 9·37 (infl.), 9·47, 9·81 10·28 (infl.), 10·39, 10·56, 11·26, 11·73, 12·24, 12·79, and 13·11 μ in agreement with the literature.[7] In the region 6·5—8 μ the maxima corresponded with those of 1-ethylnaphthalene.

Fraction F6 was chromatographed on alumina. Evaporation of the solvent and recrystallisation of the product (2 g.) from ethanol gave a hydrocarbon as prisms, m. p. 150—157°. Its ultraviolet absorption ($\lambda_{max.}$ 250, 252, 276, 288, 300, 323, 340, and 358 mμ) suggested a phenanthrene derivative, but it was not identified.

Chromatography of the residue on alumina gave 2 : 2′-dinaphthyl (1·0 g.), m. p. and mixed m. p. 182—183°; $\lambda_{max.}$ (log ε) 231 (4·12), 2·54 (4·94), and 304 (4·25) (Found: C, 94·5; H, 5·5. Calc. for $C_{20}H_{14}$: C, 94·4; H, 5·6%). Traces of 3 : 4-benzopyrene and perylene were also detected.

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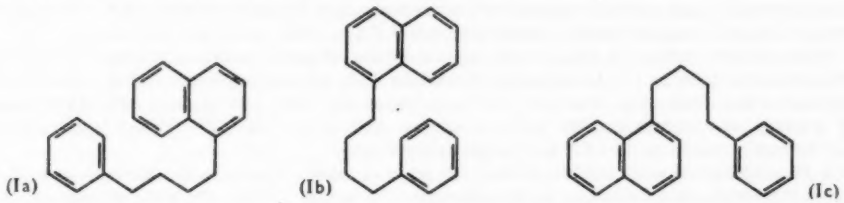
[5] Clar, *Ber.*, 1936, **69**, 1671.
[6] Clar, *Spectrochim. Acta*, 1950, **4**, 119.
[7] American Petroleum Institute Research Project 44, Infrared Spectral Data.

500. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part III.* The Pyrolysis of 1-4′-Phenylbutylnaphthalene.*

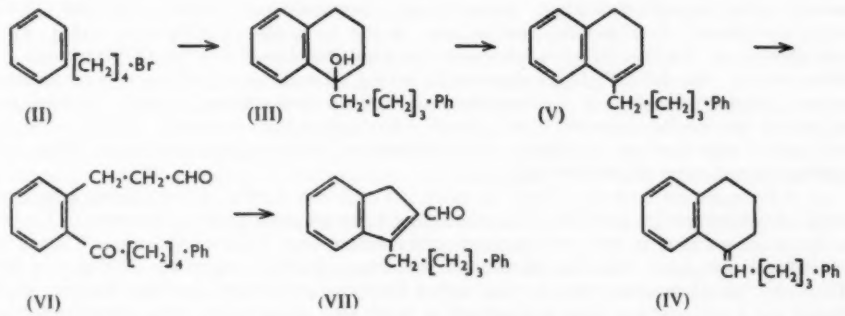
By G. M. Badger and R. W. L. Kimber.

1-4′-Phenylbutylnaphthalene (I) has been synthesised. With palladium–charcoal at 360° it gives 1-phenylphenanthrene in good yield. Cyclodehydrogenation at higher temperatures, however, gives 1 : 1′-dinaphthyl, perylene, and 3 : 4-benzopyrene in small yield.

5-4′-Phenylbutyltetralin is a possible intermediate in the formation at high temperatures of 3 : 4-benzopyrene from simple products (Parts I and II). Two mechanisms are possible: the reaction may involve a primary cyclisation, followed by dehydrogenation of the tetralin ring; or the tetralin ring may suffer simple dehydrogenation to 1-4′-phenylbutylnaphthalene (I), which could then undergo cyclodehydrogenation. The latter has now been synthesised and its dehydrogenation studied.



The cyclodehydrogenation of 1-4′-phenylbutylnaphthalene could occur in several ways: in the sense indicated by (Ia) to give 3 : 4-benzopyrene; in the sense indicated by (Ib) to give 1 : 1′-dinaphthyl and perylene; and in the sense of (Ic) to give 1-phenylphenanthrene. All these compounds have been identified as products of dehydrogenation under various conditions.



When heated with palladium–charcoal at 360° 1-4′-phenylbutylnaphthalene was converted into 1-phenylphenanthrene in 63% yield. The same product was formed in small amount, together with a little perylene, at 360° with charcoal alone. Pyrolysis at 360° in absence of catalyst gave largely unchanged material, but the fluorescence spectra of some fractions indicated the presence of a little perylene and 3 : 4-benzopyrene. Pyrolysis at 600° was more complex, and gave small yields of 1 : 1′-dinaphthyl, perylene, and 3 : 4-benzopyrene. Some cracking also occurred under most conditions, and in various experiments toluene, naphthalene, and 1-methylnaphthalene were identified.

For the synthesis of 1-4′-phenylbutylnaphthalene, ethyl β-benzoylpropionate was

* Part II, preceding paper.

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reduced to 4-phenylbutan-1-ol which was converted into the bromide (II). Its Grignard complex, or lithio-derivative, was then added to α-tetralone to give the tertiary alcohol (III). No derivative of the alcoholic function could be prepared.

Dehydration of the alcohol, which occurred very readily, could conceivably give either (IV) or (V), but ozonisation gave no tetralone. The crude product [presumably (VI)] showed two carbonyl bands in the infrared region, but treatment with acidified 2 : 4-dinitrophenylhydrazine evidently resulted in intramolecular dehydration to the dinitrophenylhydrazone of the unsaturated aldehyde (VII). A similar intramolecular dehydration to indene-2-aldehyde has been reported by Braun and Zobel.[1]

The unsaturated compound is therefore believed to be a dihydronaphthalene derivative (V). It was dehydrogenated to the desired phenylbutylnaphthalene (I) by palladium–charcoal in *p*-cymene.

Experimental

4-Phenylbutan-1-ol.—Ethyl β-benzoylpropionate [2] (100 g.), ethanol (100 c.c.), copper chromite (13 g.), and hydrogen (2000 lb./in.²) were heated at 250° for 6 hr. After 1 hr. the autoclave was cooled and the hydrogen pressure was again raised to 2000 lb./in.². Removal of catalyst and solvent gave ethyl γ-phenylbutyrate [3] (72 g., 78%), b. p. 140°/17 mm.

This product (100 g.) in ether (100 c.c.) was added dropwise to lithium aluminium hydride (30 g.) in ether (500 c.c.). After being refluxed for 1 hr. the mixture was carefully decomposed with water and dilute sulphuric acid. 4-Phenylbutan-1-ol (76 g., 96%), b. p. 124—127°/9 mm., n_D^{24} 1·5188, was obtained. Its phenylurethane had m. p. 51—52° (Braun [4] gives b. p. 140°/14 mm.; and m. p. 51—52° for the phenylurethane).

4-Phenylbutyl Bromide.—The alcohol (50 g.) was added slowly, with stirring, to a slight excess of phosphorus tribromide, under anhydrous conditions. When the addition was complete the mixture was heated (steam-bath) until reaction was complete (1½ hr.). The bromide (49 g., 72%) had b. p. 132°/12 mm., n_D^{19} 1·5408 (lit.,[5] b. p. 132°/12 mm.).

1-Hydroxy-1-4′-phenylbutytetralin.—(i) α-Tetralone (21 g.) was added dropwise to a Grignard solution prepared from phenylbutyl bromide (30 g.), magnesium (4 g.), and anhydrous ether (45 c.c.). After being refluxed for ½ hr. the mixture was poured on ice (70 g.), and 10% hydrochloric acid (100 c.c.) added. The ethereal solution was thoroughly washed (water), the ether removed, and the product distilled; three fractions were collected: (*a*) b. p. 80—100°/30 mm. (10 g.), n_D^{25} 1·5040; (*b*) b. p. 120—140°/30 mm., and (*c*) b. p. 170—172°/0·1 mm. (15 g., 37%). Redistillation of fraction (*c*) gave *1-hydroxy-1-4′-phenylbutyltetralin*, b. p. 150°/0·01 mm., n_D^{17} 1·5760 (Found: O, 5·5. $C_{20}H_{24}O$ requires O, 5·7%). Unsuccessful attempts were made to prepare a *p*-nitrobenzoate, a 3 : 5-dinitrobenzoate, and a *p*-bromophenacyl ester. In some runs analysis of the product showed that partial dehydration had occurred. Fraction (*b*) was α-tetralone. Fraction (*a*) was largely *n*-butylbenzene; further fractionation gave the pure material, identified by its infrared spectrum.[6]

(ii) 4-Phenylbutyl bromide (35 g.) in ether (50 c.c.) was slowly added (during ½ hr.) to a stirred suspension of lithium (3·5 g.) in ether (75 c.c.) in an atmosphere of nitrogen. The first few drops were added at room temperature, the mixture then being cooled to −10° until the addition was complete. The stirred mixture was then allowed to warm to +10° during 2 hr. α-Tetralone (24 g.) in ether (20 c.c.) was added dropwise at 10—20°, and the mixture finally refluxed for ½ hr. It was then filtered (glass wool) and decomposed with water and dilute hydrochloric acid. Distillation gave *n*-butylbenzene, α-tetralone, and 1-hydroxy-1-4′-phenylbutyltetralin (27 g., 57%).

3 : 4-Dihydro-1-4′-phenylbutylnaphthalene.—The above alcohol (8 g.) was dehydrated by refluxing ethanol (100 c.c.) and concentrated sulphuric acid (1 c.c.) for 1 hr. Distillation gave the *dihydrophenylbutylnaphthalene*, b. p. 174—176°/0·1 mm., n_D^{23} 1·5809 (Found: C, 91·6; H, 8·6. $C_{20}H_{22}$ requires C, 91·6; H, 8·4%), in almost quantitative yield.

[1] Braun and Zobel, *Ber.*, 1923, **56**, 2139.
[2] Kindler, *Annalen*, 1939, **452**, 90.
[3] Adkins, *Org. Reactions*, 1954, **8**, 1.
[4] Braun, *Ber.*, 1911, **44**, 2867.
[5] Clutterbuck and Cohen, *J.*, 1923, **123**, 2507.
[6] American Petroleum Institute Research Project 44, Infrared Spectral Data, Serial No. 468.

Position of unsaturation. The dihydro-naphthalene (2 g.) was ozonised in ethyl acetate (15 c.c.). Ethanol (20 c.c.) was added and the product hydrogenated over palladium–charcoal. Removal of the solvent gave a viscous oil which was separated into acid and neutral fractions. No pure derivative could be isolated from the acid fraction. The crude neutral fraction showed two peaks (5·80 and 5·93 μ) in the carbonyl region of the infrared spectrum; it gave a 2 : 4-dinitrophenylhydrazone as deep-red flat needles, (from chloroform), m. p. 210—211°. This is regarded as *3-4′-phenylbutylindene-2-aldehyde dinitrophenylhydrazone* (Found: C, 68·4; H, 5·3; O, 14·2; N, 12·4. $C_{26}H_{23}O_4N_4$ requires C, 68·6; H, 5·1; O, 14·05; N, 12·3%).

1-4′-Phenylbutylnaphthalene.—Dihydronaphthalene (14 g.) was dehydrogenated by 5 hours' refluxing with 10% palladium–charcoal (4·25 g.) in *p*-cymene (70 c.c.). Distillation gave *1-4′-phenylbutylnaphthalene* (12·5 g., 90%), b. p. 164—166/0·3 mm., n_D^{22} 1·5990 (Found: C, 92·0; H, 8·0. $C_{20}H_{20}$ requires C, 92·3; H, 7·7%); $\lambda_{max.}$ (log ε) in *cyclo*hexane 226 (4·75), 240 infl. (3·32), 264 infl. (3·56), 273 (3·78), 283 (3·81), 290 mμ (3·52). No picrate or trinitrobenzene derivative could be obtained.

Pyrolysis of 1-4′-*Phenylbutylnaphthalene.*—(i) *At* 360°. Phenylbutylnaphthalene (2 g.) was refluxed for 20 hr. and the resulting mixture chromatographed on alumina (2½ × 20 cm.). Elution with hexane gave unchanged phenylbutylnaphthalene (1·5 g.); elution with benzene–hexane (1 : 1) then gave traces of yellow crystals. The fluorescence spectra of these fractions showed bands at 398, 404, 409, 417, and 427 mμ indicative of 3 : 4-benzopyrene, and at 445, 475, and 502 mμ indicative of perylene. Fractions showing 3 : 4-benzopyrene fluorescence were combined and extracted with cold concentrated sulphuric acid.[7] The hydrocarbon was reprecipitated with water, extracted into benzene, and the benzene evaporated. The ethanolic solution of this product showed absorption maxima at 365, 384, and 405 mμ, as expected for 3 : 4-benzopyrene, the other peaks being masked by impurities.

(ii) *At* 360° *with palladium–charcoal.* Phenylbutylnaphthalene (2 g.) was refluxed with 10% palladium–charcoal (0·5 g.) for 5 hr. Chromatography on alumina and elution with hexane gave 1-phenylphenanthrene (1·25 g.), prisms, m. p. 78—79° (lit.,[8] m. p. 78—79°) (from light petroleum) (Found: C, 94·6; H, 5·7. Calc. for $C_{20}H_{14}$: 94·5; H, 5·5%); $\lambda_{max.}$ (log ε) in ethanol 220 (4·46), 256 (4·72), 290 (4·08), 300 (4·16), 334 (2·64), 342 (2·49), and 350 mμ (2·52). Its picrate had m. p. 117—118° (lit.,[8] m. p. 117—118°) (Found: N, 8·8. Calc. for $C_{26}H_{17}O_7N_3$: N, 8·7%). Further elution of the column with benzene–hexane (1 : 2) gave fractions showing faint fluorescence spectra identical with those of 3 : 4-benzopyrene and of perylene.

(iii) *At* 360° *with charcoal.* Phenylbutylnaphthalene (2 g.) was refluxed with activated charcoal (0·5 g.) for 5 hr. Rearrangement of the apparatus for distillation gave some distillate (200 mg.), b. p. <220°. Recrystallisation gave naphthalene (100 mg.), m. p. and mixed m. p. 79·5—80°. The remainder of the product was chromatographed on alumina. Elution with hexane gave 1-phenylphenanthrene (150 mg.) identified by direct comparison with the specimen obtained above. Elution with benzene–hexane (1 : 2) of a blue fluorescent band and recrystallisation of the residue gave perylene as yellow prisms, m. p. and mixed m. p. 265°, further identified by comparison of its fluorescence spectrum with that of an authentic specimen. No benzopyrene was detected.

(iv) *At* 360° *with palladium–asbestos.* Phenylbutylnaphthalene (2 g.) was refluxed with 5% palladium–asbestos (1 g.) for 5 hr. A low-boiling fraction was mainly toluene, b. p. 110°, n_D^{25} 1·4913 (infrared spectrum). Chromatography on alumina (3 × 15 cm.) and elution with hexane gave 8 fractions (each of 70 c.c.). Further elution with benzene–hexane (1 : 2) gave fractions 9—18 (each of 70 c.c.). Fraction 1 yielded unchanged phenylbutylnaphthalene. Fractions 2—7 showed diffuse fluorescence at 400—480 mμ. The later fractions showed fluorescence bands indicative of 3 : 4-benzopyrene and perylene. Fraction 8 gave an ultraviolet spectrum similar to that of a chrysene derivative. Fractions 9 and 10 showed some of the same maxima as fraction 8 and also bands suggestive of perylene and 3 : 4-benzopyrene.

(v) *At* 600°. Phenylbutylnaphthalene (5 g.) was vapourised at the rate of 1 drop/15 sec. and passed with nitrogen (1 c.c./sec.) through a silica tube (36 × 1 in.) packed with porcelain chips (3/8—1/4 in.) heated to 600°. Distillation of the resulting tar gave (*a*) b. p. 110—120° (1·25 g.), (*b*) b. p. 90—120°/28 mm. (1·5 g.), and (*c*) the residue (1·5 g.).

Fraction (*a*) was mainly toluene, identified by refractive index and infrared spectra. Fraction (*b*) was heated (boiling-water bath) at atmospheric pressure and naphthalene (0·1 g.),

[7] Berenblum, *Nature*, 1945, **156**, 601.
[8] Bachmann and Wilds, *J. Amer. Chem. Soc.*, 1938, **60**, 624.

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m. p. and mixed m. p. 80°, sublimed. The yellow liquid remaining was redistilled, yielding 1-methylnaphthalene, identified by ultraviolet and infrared spectroscopy and by refractive index. The picrate had m. p. and mixed m. p. 140—142°.

Fraction (*c*) was chromatographed on alumina (2½ × 20 cm.). A blue fluorescent band was eluted with hexane (fractions 4—8; each of 70 c.c.), then an orange fluorescent band with benzene–hexane (1 : 1) (fractions 9—10; each of 70 c.c.), and finally a yellow fluorescent band with benzene (fractions 11—12; each of 70 c.c.).

Fractions 4 and 5 were combined and rechromatographed in hexane. Evaporation of the first fractions yielded a solid (20 mg.), with ultraviolet absorption spectrum identical with that of 1 : 1′-dinaphthyl; but it could not be obtained pure, having m. p. 143—146° alone, and 145° mixed with an authentic specimen (m. p. 145°). Further elution of this chromatogram with benzene–hexane (1 : 2) gave a pale yellow solid (10 mg.), $\lambda_{max.}$ in ethanol 240, 261, 272, 304, 319, and 334 mμ, indicative of pyrene.[9]

Fractions 6—9 were combined and twice rechromatographed on a large column of alumina, hexane and benzene–hexane being used as eluants. The first fractions contained a mixture of perylene and 3 : 4-benzopyrene. The fluorescence spectra showed bands associated with both hydrocarbons: $\lambda_{max.}$ in ethanol 434, 429 infl., 408, and 386 mμ associated with perylene,[9] and at 225, 296, 348, and 364 mμ associated with 3 : 4-benzopyrene.[9] Later fractions contained more 3 : 4-benzopyrene; one showed maxima at 226, 255, 266, 273, 284, 296, 330, 347, 364 infl., 378, 384, 404 mμ as expected for 3 : 4-benzopyrene;[9,10] and also gave a 3 : 4-benzopyrene fluorescence spectrum. Evaporation of the solvent gave almost pure 3 : 4-benzopyrene, m. p. and mixed m. p. 170—172° (lit.,[9] m. p. 176·5—177·5°). The total estimated quantity of perylene was 3 mg. and of 3 : 4-benzopyrene 10 mg.

Similar results were obtained following pyrolysis of phenylbutylnaphthalene at 700°, except that the yield of naphthalene (2 g.) was much greater. Pyrolysis at 500° was much less effective and gave 3·5 g. of unchanged material (from 5 g.).

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[9] Clar, "Aromatische Kohlenwasserstoffe," 2nd edn., Springer, Berlin, 1952.
[10] Mayneord and Roe, *Proc. Roy. Soc.*, 1935, *A*, **152**, 323.

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501. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part IV.* The Pyrolysis of Styrene.*

By G. M. BADGER and R. G. BUTTERY.

Pyrolysis of styrene at 710° gives a complex mixture of products.

PYROLYSIS of butadiene [1] yields relatively large quantities of styrene and ethylbenzene, and the further pyrolysis of these products is of interest. Berthelot [2] found that styrene gave acetylene and benzene when passed through a porcelain tube at bright-red heat, but the temperature seems to be critical. A 99% recovery of styrene has been reported [3] following heating at 550°, and 95·3% after heating [4] at 625°. At higher temperatures there is much more "decomposition," but little attempt has been made to examine the products. The pyrolysis of styrene has now been investigated to determine whether it can act as an intermediate in the formation of polycyclic aromatic hydrocarbons, such as 3 : 4-benzopyrene, at high temperatures.

Styrene vapour, with nitrogen, was passed through a silica tube, filled with porcelain chips, at 710°. The resulting tar was analysed by distillation, spectra, and gas-liquid partition chromatography. In this way all the major products having boiling points below that of pyrene, and formed in more than 0·2% yield, have been identified:

* Part III, preceding paper.

[1] Weizmann *et al.*, *Ind. Eng. Chem.*, 1951, **43**, 2312, 2318.
[2] Berthelot, "Les Carbures d'Hydrogène," Gauthier-Villars, Paris, 1901.
[3] Mackinnon and Ritchie, *J.*, 1957, 2564.
[4] Balandin, Marukyan, and Tolstopyatove, *Zhur. priklad. Khim.*, 1946, **19**, 1079; Balandin and Tolstopyatova, *Zhur. obshchei Khim.*, 1947, **17**, 2182.

Methane (—), ethylene (—), benzene (6·4), toluene (3·3), ethylbenzene (1·6), indene (0·4), naphthalene (6·1), methylnaphthalenes(?) (0·2), diphenyl (1·6), dibenzyl (0·9), fluorene (1·3), stilbene (1·3), phenanthrene (11·1), anthracene (0·3), 2-phenylnaphthalene (2·5), a pyrene-containing fraction, b. p. 220—250°/21 mm. (1·9), a chrysene-containing fraction, b. p. 250—265°/21 mm. (3·3), and a C_{20}-fraction, b. p. 265—315°/21 mm. (4·6), which contained 3 : 4-benzopyrene (*ca.* 0·02) (values in parentheses are percentage yields, by weight).

Contrary to the findings by Berthelot, no acetylene could be detected. Addition of aniline and phenol is known to inhibit the " decomposition " of styrene,[4] and there can be little doubt that the high-temperature reactions leading to the formation of these products are predominantly radical. It is therefore important to determine which bonds are most likely to break to yield radicals.

From consideration of bond-dissociation energies [5] for various types of carbon–hydrogen and carbon–carbon bonds, it seems likely that the carbon–hydrogen bonds in styrene all have bond-dissociation energies of the order of 100 kcals. If account is taken of their bond orders,[6] approximate values for the bond-dissociation energies for the carbon–carbon bonds can also be obtained. Thus the carbon–carbon double bond probably has a bond-dissociation energy of *ca.* 140 kcals., and the carbon–carbon single bond linking the ethylenic group to the benzene ring, a bond dissociation energy of *ca.* 110 kcals. There is thus little difference in the energy required to break any C–H bond and the carbon–carbon single bond; but a much greater energy is required to break the carbon–carbon double bond (or the aromatic ring). This leads to the conclusion that the most important radicals may be Ph·, ·$CH{=}CH_2$, Ph–$CH{=}CH$·, Ph–$\dot{C}{=}CH_2$, and ·C_6H_4–$CH{=}CH_2$.

Such radicals could undergo a variety of reactions, both chain-propagating and chain-terminating. Reaction 1 would explain the formation of stilbene. If it is assumed that cyclisation to an aromatic system would readily follow, then reactions (1—4) would offer satisfactory schemes for the observed relatively high yields of phenanthrene, naphthalene, and 2-phenylnaphthalene. It may here be noted that phenanthrene is formed when stilbene is passed through a red-hot tube,[7] and naphthalene is formed by the pyrolysis of phenylbutadiene [8] and other similar hydrocarbons. The known interconversion of phenanthrene and anthracene [9] at high temperature could account for the small yield of anthracene.

$$Ph{-}CH{=}CH\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH{-}Ph + CH_2{=}CH\cdot \quad (1)$$

$$Ph{-}CH{=}CH\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH{-}CH{=}CH_2 + Ph\cdot \quad (2)$$

$$Ph{-}CH{=}CH\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH{-}\underset{\displaystyle Ph}{\underset{|}{C}}{=}CH_2 + H\cdot \quad (3)$$

$$Ph{-}CH{=}CH\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH{-}C_6H_4\cdot + CH_2{=}CH_2 \quad (4)$$

The propagation of this radical chain could result by reactions such as (5—7). The large yield of benzene and the predominance of ethylene among the gaseous products would indicate the importance of such collisions.

$$Ph\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH\cdot + PhH \quad (5)$$

$$CH_2{=}CH\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH\cdot + CH_2{=}CH_2 \quad (6)$$

$$H\cdot + Ph{-}CH{=}CH_2 \longrightarrow Ph{-}CH{=}CH\cdot + H_2 \quad (7)$$

Diphenyl could be formed by a chain-terminating reaction involving two phenyl radicals, or more probably, by a chain propagating reaction of a phenyl radical with a styrene molecule.

[5] Braude and Nachod, " Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955; Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1954.
[6] Buu-Hoï, Coulson, Daudel, Daudel, Martin, Pullman, and Pullman, *Rev. Sci.*, 1947, **85**, 1041.
[7] Graebe, *Ber.*, 1873, **6**, 125; see also Zelinsky and Titz, *Ber.*, 1929, **62**, 2869.
[8] Liebermann and Riiber, *Ber.*, 1902, **35**, 2697.
[9] Orlow, *Ber.*, 1927, **60**, 1950.

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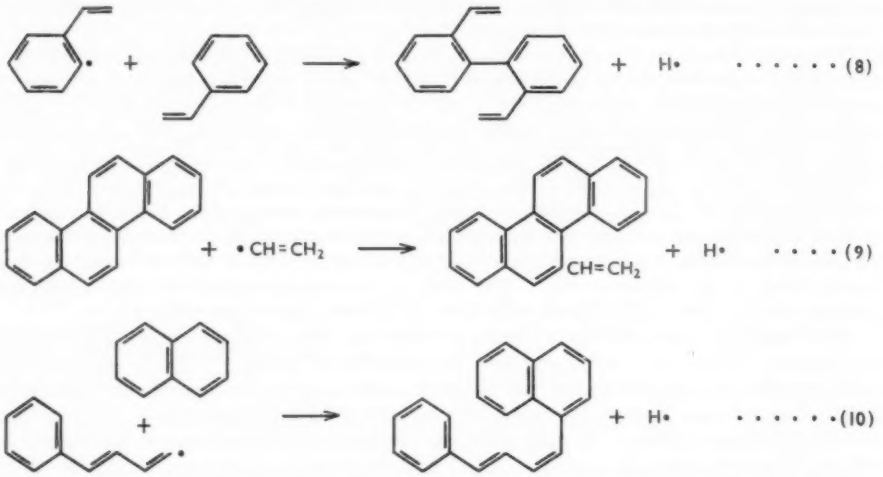
Toluene is the only methylated hydrocarbon of which more than a trace is formed and this is probably formed in a secondary reaction. Thus reduction of stilbene would give dibenzyl, the central bond of which has a very small bond-dissociation energy.[10] Fission would give two benzyl radicals, and toluene could then be formed by chain termination or propagation. Similarly fluorene could result by reaction of a benzyl radical with a phenyl radical (to give diphenylmethane), followed by cyclodehydrogenation. Pyrolysis of diphenylmethane yields fluorene.[11] The benzyl radical may also be involved in the formation of indene. Thus reaction of ethylene, or a vinyl radical, with a benzyl radical, followed by cyclohydrogenation would give this hydrocarbon.



Chrysene is obtained in good yield by the pyrolysis of indene,[12] and the chrysene detected is probably formed in this way.

Pyrene may be formed in a manner similar to that suggested by Weizmann *et al.*,[1] *i.e.*, eqn. (8), followed by cyclodehydrogenation. An analogous synthesis [13] by catalytic cyclodehydrogenation of di-*m*-xylylene is of interest. However, the small yield of pyrene indicates that this cannot be an important reaction.

3 : 4-Benzopyrene was a product of the pyrolysis of styrene but only in small amount, and no decision can be made regarding its method of formation. Two reactions seem probable. The first would involve the attack of a vinyl radical on chrysene [eqn. (9)] followed by cyclodehydrogenation; there are four positions at which the vinyl radical could possibly attack chrysene and lead to 3 : 4-benzopyrene. The second mechanism would involve the reaction of a phenylbutadiene radical with naphthalene [eqn. (10)], and cyclodehydrogenation of the product. Phenylbutadiene was not identified, but this could well be due to its reactivity and instability at the reaction temperature. Its conversion into naphthalene has been established; moreover, an unidentified product (0·2% yield) had a retention time close to that of *n*-butylbenzene, and this is the expected product from the reduction of phenylbutadiene.

Experimental

Styrene.—Styrene (Reichhold Chemicals Inc.) was distilled through a 15-cm. Vigreux column, and had b. p. 81°/90 mm., n_D^{25} 1·5440 (lit. n_D^{23} 1·5440). Gas–liquid partition chromatography did not detect ethylbenzene.

[10] Horrex and Miles, *Discuss. Faraday Soc.*, 1951, **10**, 187.
[11] Graebe, *Ber.*, 1873, **6**, 127; *Annalen*, 1874, **174**, 185.
[12] Spilken, *Ber.*, 1893, **26**, 1538.
[13] Baker, McOmie, and Norman, *J.*, 1951, 1114.

Pyrolysis of Styrene at 710°.—Styrene (100 g.) was vaporised by adding it dropwise (1 drop/8 sec.; 10 g./hr.) to a Pyrex tube immersed in a lead bath at 340°, and carried in a stream of nitrogen (30 c.c./min.) into the furnace at 710°. The vapours leaving the furnace were passed through an air-condenser and an efficient vertical water-condenser, and finally through a trap of solid carbon dioxide. The average yield of liquid was 84 g., and more (1 g.) was obtained by washing the pyrolysis tube with benzene, followed by evaporation of the benzene. The gaseous products gave no precipitate with ammoniacal cuprous bromide but decolorised aqueous permanganate. Samples of gaseous product were examined in the infrared spectrometer.

Gas–liquid chromatographic analysis.

Fraction	B. p.°/mm.	Conditions * A	B	C	D	Product	Retention time min.	sec.
I	40—70/110	113°	0·7	—	atmos.	benzene	2	50
						toluene	6	30
						ethylbenzene	12	—
						styrene	16	—
II	65—92/30	175°	0·7	—	atmos.	styrene	3	30
						indene	9	20
						naphthalene	23	10
III	92—134/24	169	—	220	18	naphthalene	6	50
						diphenyl	17	40
IV	134—185/21	220	—	230	18	naphthalene	2	30
						diphenyl	5	20
						dibenzyl	9	10
						fluorene	16	10
						stilbene	24	10
V	185—220/21	265	—	200	18	fluorene	6	20
						phenanthrene	14	40
						pyrene	52	30
						chrysene	*ca.* 2 hr.	

* *A*, temperature. *B*, flow rate, c.c./sec. *C*, initial pressure. *D*, outlet pressure.

Details of Chromatographic Analysis.—The tar was fractionally distilled at reduced pressure in a 30 cm. electrically heated, jacketed, unpacked column. Some fractions were examined separately, but for the major chromatographic analysis several were combined to form five main fractions. Each main fraction was then submitted to gas–liquid chromatography as specified in the Table, which also gives the retention times for the major components of each fraction.

The compositions were determined by comparison of areas under the peaks in the chromatographic curves. The method of multiplying peak height by peak width at half-peak height was used. Each component was checked by using known mixtures and tests over a wide range of composition showed most determinations to be within 7% of the true value, with a maximum error of 11%. Anthracene has the same retention time as phenanthrene and its proportion was determined by ultraviolet spectroscopy. The results are summarised in the Introduction.

Details of Identification.—Methane and ethylene. Gaseous products from the furnace were passed into an 11-cm. gas cell for infrared analysis. Methane was identified by its characteristic spectrum [14a] in the 7·5—8·5 μ region (maxima at 7·65, 7·7, 7·75, 7·78, 7·82, 7·86, 7·92, 7·95, 8·00, 8·03, 8·05, 8·13, 8·18, and 8·26). Ethylene was identified by its characteristic spectrum [14b] in the 9·0—11·5 μ region (maxima at 9·93, 10·02, 10·13, 10·22, 10·3, 10·53, 10·63, 10·76, 10·84, 10·93, 11·01, 11·07, 11·16, and 11·25 μ). There were also other bands characteristic of ethylene in other regions. The furnace gases decolorised neutral permanganate.

Benzene. A fraction, b. p. 80—84°, was examined in the infrared region; maxima at 2·14, 2·44, 2·72, 3·25, 3·76, 3·84, 4·18, 4·27, 4·48, 5·08, 5·5, 5·7, 5·82, 5·97, 6·23, 6·55, 6·8, 7·19, 8·02, 8·5, 9·5, and 9·7 μ were characteristic of benzene; [14c] some peaks characteristic of toluene were also identified.

Toluene. The fraction, b. p. 90—100°, gave maxima at 2·15, 2·44, 2·72, 3·26, 3·4, 3·45, 3·65,

[14] American Petroleum Institute Research Project 44, Infrared Spectral Data (*a*) No. 528; (*b*) No. 18; (*c*) No. 307; (*d*) No. 308; (*e*) No. 170.

3·85, 4·28, 4·5, 5·10, 5·36, 5·5, 5·76, 6·25, 6·35, 6·57, 6·8, 7·25, 7·5, 7·61, 8·03, 8·30, 8·50, 9·05, 9·28, 9·7, 10·1, 11·0, and 11·85 μ characteristic of toluene; [14d] some peaks characteristic of benzene were also noted.

Ethylbenzene. This was identified only by the ratio of its retention time to that of benzene (4·5). *m*- and *p*-Xylene under the same conditions gave corresponding ratios of 5·1 and *o*-xylene had a higher ratio.

Styrene. Isolated from fraction (I) this had n_D^{15} 1·5490 (lit. $n_D^{16\cdot6}$ 1·5485) and gave maxima at 2·4, 3·2, 3·22, 5·04, 5·28, 5·44, 5·68, 5·89, 6·1, 6·21, 6·31, 6·5, 6·68, 6·85, 7·04, 7·45, 7·55, 7·72, 8·3, 8·45, 8·65, 9·0, 9·2, 9·28, 10·08, 11·0, 11·9, 12·9, and 14·35 μ, in agreement with the literature.[14e] The isomeric xylenes have retention times similar to that of styrene. However, the absence of the strong maxima at 11·5, 12·5, and 13·5 μ in the infrared spectrum indicates the absence of *m*-, *p*-, and *o*-xylene, respectively.

Indene. This was isolated from fraction (II). In carbon tetrachloride it showed maxima at 3·19, 3·26, 3·32, 3·39, 3·47, 3·63, 5·15, 5·22, 5·3, 5·35, 5·39, 5·48, 5·57, 5·77, 5·86, 5·92, 6·04, 6·22, 6·87, 7·2, 7·48, 7·8, 8·05, and 8·35 μ, in agreement with those obtained on an authentic specimen.

Naphthalene. Isolated from fraction (II), this had m. p. and mixed m. p. 79—80°.

Methylnaphthalenes. Gas–liquid chromatography of the fraction, b. p. 98—134°/24 mm., under the conditions used for fraction (III) showed a minor broad band with ratio of retention time of 2·0 compared to that of naphthalene. An authentic mixture of 1- and 2-methylnaphthalene gave the same ratio.

Diphenyl. This was isolated from fraction (III). In carbon tetrachloride it showed maxima at 2·46, 3·27, 3·30, 3·42, 3·48, 5·10, 5·14, 5·26, 5·31, 5·35, 5·49, 5·55, 5·49, 5·55, 5·68, 5·74, 5·95, 6·04, 6·78, 6·88, 6·99, 7·26, 7·74, 7·97, and 8·16 μ, in agreement with those shown by an authentic specimen.

Dibenzyl. In carbon tetrachloride this showed maxima at 2·4, 3·25, 3·37, 3·45, 5·1, 5·29, 5·5, 5·65, 5·9, 6·75, 6·90, 6·99, 7·08, 7·21, 7·5, 7·62, 8·5, 9·34, 9·75, 10·85, and 11·3 μ. Authentic dibenzyl showed maxima at all these wavelengths except 6·99, 7·08, and 7·62 μ. The shapes of the spectra were very similar, but the fraction isolated showed reinforcement of some bands. Diphenyl is a probable impurity.

Fluorene. The fluorene sample had ultraviolet spectra maxima at 300, 290, and 260 mμ. Clar [15] gives maxima at 300·5, 289, and 261 mμ.

Stilbene. This was isolated from fraction (IV) by chromatography at 265° (as for fraction V), (retention time 8 min. 50 sec.), and had m. p. and mixed m. p. 124·5—125°; $\lambda_{max.}$ at 220, 295, and (infl.) 307 mμ (literature [15] max. at 295 infl. at 307 mμ).

Anthracene and phenanthrene. A mixture was isolated (retention time 14 min. 40 sec.) from the fraction, b. p. 192—198°/21 mm., by chromatography at 265° under vacuum. Its ultraviolet absorption spectrum in 95% ethanol showed maxima at 252·5, 275, and 292·5 mμ (characteristic of phenanthrene) and at 340, 357·5, and 375 mμ, with inflexions at 310, 325, and at 371 mμ (characteristic of anthracene). The proportion of anthracene was estimated from the intensity of the band at 375 mμ. Recrystallisation gave substantially pure phenanthrene, m. p. and mixture m. p. 96—100°.

2-*Phenylnaphthalene.* This was isolated (retention time 24 min. 54 sec.) from the fraction, b. p. 192—198°/21 mm., by chromatography at 265° under vacuum. It had m. p. 99·5—101°, undepressed by admixture with an authentic specimen.

Pyrene. The crude fraction, b. p. 215—220°/21 mm., showed $\lambda_{max.}$ at 375, 357·5, 335, 319, 292·5, 272·5, 255, and 242·5 mμ. Peaks at 335, 319, 272·5, and 242·5 mμ are characteristic of pyrene.

The crude fraction was treated with picric acid in ethanol; the complex after recrystallisation had m. p. and mixed m. p. 215—218°. Tetrabromopyrene, prepared from the crude fraction in nitrobenzene, had m. p. and mixed m. p. 400—402°.

Chrysene. Part of the fraction, b. p. 250—264°/21 mm. (0·393 g.), was recrystallised from glacial acetic acid, yielding substantially pure chrysene (0·03 g.); $\lambda_{max.}$ 360, 340, 317·5, 305, 295, 285, 267·5, 257·5, 240, and 220 mμ. Except for that at 340 mμ, these maxima are characteristic of chrysene.[15]

3 : 4-*Benzopyrene.* The fraction, b. p. 300—310°/21 mm. (4 g.), was dissolved in benzene (50 c.c.) and shaken with concentrated sulphuric acid (50, 40, then 30 c.c.) at 5°. The sulphuric

[15] Clar, " Aromatische Kohlenwasserstoffe," 2nd Edn., Springer, Berlin, 1952.
[16] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951.

acid solution was poured on ice (150 g.), and water (150 c.c.) added.[17] The mixture was then extracted with benzene, and the solution washed, dried, and concentrated to 20 c.c. Hexane (20 c.c.) was then added and the solution chromatographed on alumina, hexane–benzene (2 : 1) being used as eluant. Those fractions showing fluorescence in the region characteristic for 3 : 4-benzopyrene were combined and evaporated. The resulting solid (0·19 g.) was crude 3 : 4-benzopyrene; it showed characteristic fluorescence bands at 404, 433, and 456 mμ (in light petroleum), and ultraviolet absorption maxima at 404, 385, 365, 345, 319, 295, 285, 267·5, 257·5, and 225 mμ (in 95% ethanol). With the exception of the bands at 319, 267·5, and 257·5 mμ (chrysene?), these are characteristic of 3 : 4-benzopyrene.[16]

UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA. [*Received, January 24th*, 1958.]

[17] Berenblum, *Nature*, 1945, **156**, 601.

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502. *Infrared Spectra and Polar Effects. Part VIII.*† *The Frequencies and Stabilities of Olefinic Systems.*

By L. J. BELLAMY and R. L. WILLIAMS.

The C=C stretching frequencies of non-conjugated hydrocarbons are related to the enthalpies of hydrogenation and indirectly to Taft's σ^* reactivity constants of the substituents. A similar relation connects the heats of chlorination of fluorinated olefins with the frequencies but the direction of slope of the resulting line is inverted. The reasons for this are discussed in terms of the factors responsible for the group frequency shifts.

THE most useful infrared group frequencies for structural work are those arising from X–H modes and from the stretching motions of multiple bonds. This is because changes of mass in the substituents lead to only very small frequency shifts, whilst the high initial frequencies reduce the incidence of mechanical coupling. For the carbonyl vibration, for example, Halford [1] has shown that the >C=O stretching frequencies are insensitive to mass changes of the substituents for all masses greater than 12, and similar treatments are available for the C≡N [2] and C≡C [3] vibrations. Despite this freedom from mass effects the frequencies of multiple bonds vary widely. The carbonyl absorption, for example, occurs near 1600 cm.$^{-1}$ in compounds such as acetonylacetone [4] but rises as high as 1928 cm.$^{-1}$ in COF_2,[5] and possibly to 2305 cm.$^{-1}$ in $CH_3{\cdot}COCl,AlCl_3$.[6] These shifts are due to inductive and mesomeric effects of the substituents [7] together with intramolecular-field effects in special cases.[8] This suggests that the frequency shifts of such vibrations should correlate directly with changes in other physical properties which depend directly upon the same factors. Many such correlations are summarised in ref. 7. They are interesting because of the light they throw on the origins of group-frequency shifts and of the possibility that selected frequency shifts may afford a better measure of the relative magnitudes of polar effects than any other which is yet available.

The commonest examples of relationships between physical properties and group-frequency shifts are those which connect the latter with Hammett's σ reactivity constants,[7] and in some instances the band intensity has been related to the same function.[9] The reactions chosen for such comparisons need to be selected with great care as the kinetics

† Part VII, *J.*, 1957, 4294.

[1] Halford, *J. Chem. Phys.*, 1956, **24**, 830.
[2] Whiffen, *Chem. and Ind.*, 1957, 193.
[3] Lord and Miller, *Appl. Spectroscopy*, 1956, **10**, 115.
[4] Bellamy and Beecher, *J.*, 1954, 4487.
[5] Kagarise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.
[6] Susz and Wuhrmann, *Helv. Chim. Acta*, 1957, **40**, 971.
[7] Bellamy, *J.*, 1955, 4221.
[8] Bellamy and Williams, *ibid.*, 1957, 4294.
[9] Steel and Thompson, *Trans. Faraday Soc.*, 1956, **52**, 1451.

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of a reaction involving electromeric effects in which the reactant is first polarised by the reagent are not likely to be related to the frequencies of the ground state. However Taft's work [10] on σ^* reactivity constants represents an important advance in this respect, enabling Hammett-type relationships to be used in the aliphatic series, and it has recently been shown that σ^* values for the appropriate substituents correlate directly with the carbonyl and nitroso-group frequencies of such materials.[11]

Taft and Kreevoy [12] successfully showed that a relationship exists between the enthalpies of hydrogenation of non-conjugated olefins and the σ^* values of their substituents. This is subject to limitations in some cases owing to steric factors, and it seemed of interest to see whether the >C=C< frequencies correlated with the same functions, particularly as steric effects would not always have the same effect in the two cases. This study has been extended to a comparison of the frequencies and heats of chlorination of fluorinated olefins which are spectroscopically anomalous in having abnormally high C=C frequencies. The possibility of relations between the frequencies of cyclic olefins and the equilibrium constants for π-complex formation has also been considered.

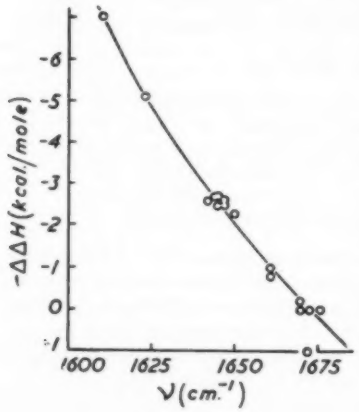


FIG. 1.

Enthalpies of Hydrogenation.—The enthalpies of hydrogenation of a series of olefins are listed at Table 1, together with the corresponding C=C stretching frequencies. Fig. 1 shows that a smooth relation exists. As Taft and Kreevoy [12] have shown that these enthalpies are directly related to σ^* values by the expression $\Delta\Delta H = (\Sigma\sigma^*)\rho^* + (\Delta n)h$, this indicates that the frequencies will likewise correlate with the reactivities. Some similarities and differences between these two approaches are noteworthy. In neither case have conjugated compounds been included because the resonance-energy term so introduced is not wholly reflected either in the infrared frequencies or in the σ^* values. However, Taft [12] also reported that the enthalpies of *cis*- and vicinally disubstituted ethylenes also failed to correlate with σ^* values and he attributed this to steric effects. Although the data are limited, this appears not to be true of the infrared frequencies. The points for both *cis*-but-2-ene and *iso*butene lie on the line of Fig. 1, and even for 2 : 3-dimethylbut-2-ene the discrepancy is only 1 kcal./mole. Further the C=C stretching frequencies of *cis*-isomers are known to be consistently lower than those of the *trans*-forms, in accordance with the observed enthalpies. In cyclic systems however neither the frequencies nor the σ^* values are related to the observed enthalpies because the latter now include additional terms involving the change in the geometry of the ring and the numbers of eclipsed CH_2 groups. The frequency for *cyclo*hexene, for example, corresponds to a value on Fig. 1 of −5·0 kcal./mole whereas the observed enthalpy is only −1·0 kcal./mole. For conjugated systems Taft [12] suggests that the degree of divergence from the calculated value measures the extra resonance energy. The divergence for styrene (1630 cm.$^{-1}$) is −5·3 kcal./mole which agrees reasonably well with Taft's value of −4·3.

One point of particular interest arises in connection with the direction of slope of this line. On passing from vinyl chloride to *trans*-but-2-ene, the C=C frequency rises. We suggest that this is due to an increase in the covalency of the multiple bond as the contributions of polar forms such as (I) are reduced. This should increase the stability of

[10] Taft, "Steric Effects in Organic Chemistry," Wiley, New York, 1956.
[11] O'Sullivan and Sadler, *J.*, 1957, 4144.
[12] Taft and Kreevoy, *J. Amer. Chem. Soc.*, 1957, **79**, 4011.

the olefinic bond, and is therefore consistent with the direction of the change of the enthalpy. However *trans*-but-2-ene has an almost wholly covalent bond and therefore

(I) $CH_3\overset{-}{C}H=\overset{+}{C}l$ $\qquad$ $F\diagdown\overset{+}{C}=CH_2$ (II) $\quad -F$

represents an end to this process. Any further rise in the C=C frequency can then only come about through the introduction of acetylenic character which would involve contributions from canonical forms such as (II). Hence, continuation of the line of Fig. 1 beyond 1675 cm.$^{-1}$ would lead to a reversal in direction so that any increase in frequency

FIG. 2.

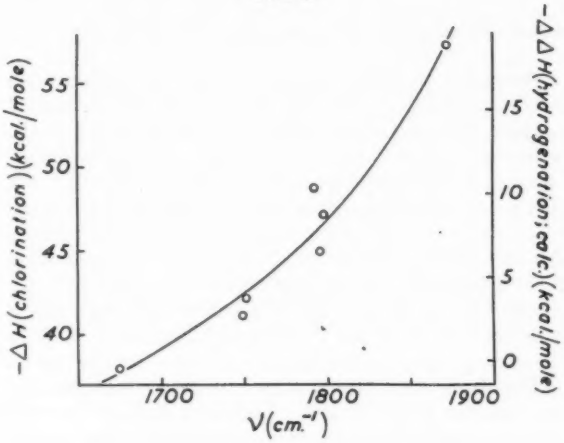
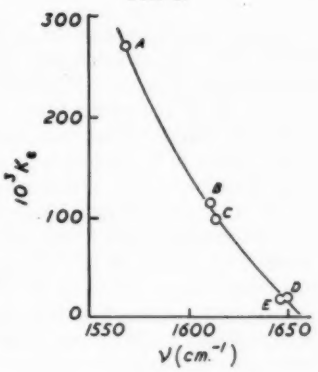


FIG. 3.



would be accompanied by an increase in enthalpy. This possibility has been explored by comparing heats of chlorination of such compounds with their frequencies.

Heats of Chlorination of Fluorinated Olefins.—Reaction of fluoro-olefins with hydrogen does not give the saturated product and hydrogen fluoride is usually displaced, so heats of hydrogenation cannot be measured directly. However, fluoro-olefins are directly

TABLE 1. *Stretching frequencies of the ethylenic bond (cm.$^{-1}$) and enthalpies of hydrogenation ($\Delta\Delta H°$ at 355° K; kcal./mole).*

Compound	ν [a]	$\Delta\Delta H$ [b]	Compound	ν [a]	$\Delta\Delta H$ [b]	Compound	ν [a]	$\Delta\Delta H$ [b]
Ethylene ...	1623	−5·2	3-Methylbut-1-ene	1644	−2·7	*trans*-Hex-2-ene ...	1670	0
Propene ...	1647	−2·5	3 : 3-Dimethylbut-1-ene	1645	−2·7	*iso*Butene	1661	−0·8
But-1-ene	1645	−2·7	*trans*-But-2-ene	1676	0	2 : 3-Dimethylbut-		
Pent-1-ene	1647	−2·6	*cis*-But-2-ene	1661	−1·0	2-ene	1672	+1·0
Hex-1-ene	1642	−2·6	*trans*-Pent-2-ene	1673	0	Vinyl chloride	1610 [e]	−7·0 [d]
Hept-1-ene	1645	−2·5	*trans*-4-Methylpent-2-ene	1670	−0·2	Diethyl fumarate ...	1650 [e]	−2·3 [f]

[a] From Sheppard and Simpson, *Quart. Rev.*, 1952, **6**, 1, except where stated. [b] From ref. 12 except where other references given; based on *trans*-but-2-ene = −27·6 kcal./mole. [c] Torkington and Thompson, *J.*, 1944, 303. [d] Lacher, Kianpour, Oetting, and Park, *Trans. Faraday Soc.*, 1956, **52**, 1506. [e] Walton and Hughes, *J. Amer. Chem. Soc.*, 1957, **79**, 3985. [f] Turner and Meacher, *ibid.*, p. 4133.

chlorinated, and some thermochemical data are available (see Table 2 and Fig. 2) which, though few, suggest another smooth relation; the enthalpies rise with frequency as suggested above. For comparison we can compute the theoretical enthalpies of hydrogenation of these compounds through the known heats of chlorination and hydrogenation of ethylene, and such values form the right-hand scale of Fig. 2; extrapolation of the line

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would intersect the corresponding line of Fig. 1 near 1675 cm.$^{-1}$ and zero enthalpy, this being the frequency of a purely covalent olefinic bond of maximal stability.

TABLE 2. *Heats of chlorination (at 411° K, kcal./mole) and stretching frequencies of the ethylenic bond (cm.$^{-1}$).*

Compound	ΔH [a]	ν	Compound	ΔH [a]	ν
$CH_2{:}CH_2$	−43·6 [b]	1623 [c]	$CF_2{:}CF{\cdot}C_2F_5$	−44·96	1795 [e]
$CF_2{:}CF_2$	−57·32	1872 [d]	$CF_2{:}CCl_2$	−41·07	1749 [e]
$CF_2{:}C(CF_3)_2$	−42·22	1751 [e]	$CF_2{:}CFCl$	−48·81	1792 [b]
$CF_2{:}CF{\cdot}CF_3$	−47·15	1797 [f]	*trans*But-2-ene	−38·4 (calc.)	1676

[a] Lacher, Kianpour, and Park, *J. Phys. Chem.*, 1957, **61**, 584. [b] Konn, Kistiakowsky, and Smith, *J. Amer. Chem. Soc.*, 1938, **60**, 2764. [c] Sheppard and Simpson, *Quart. Rev.*, 1952, **6**, 1. [d] Nielsen, Claasen, and Smith, *J. Chem. Phys.*, 1950, **18**, 812. [e] Brice, Lazerte, Hals, and Petersen, *J. Amer. Chem. Soc.*, 1953, **75**, 698. [f] Nielsen, Claasen, and Smith, *J. Chem. Phys.*, 1952, **20**, 1916. [g] *Idem*, *ibid.*, 1950, **18**, 485. [h] Mann, Aquista, and Plyler, *J. Res. Nat. Bur. Stand.*, 1954, **52**, 1792.

Cyclic Compounds.—The C=C frequencies of cyclic compounds such as *cyclo*pentene, *cyclo*butene, etc., do not obey the relation of Fig. 1, nor does the heat of chlorination of perfluoro*cyclo*butene (−37·4 kcal./mole) correspond to the observed frequency (1785 cm.$^{-1}$). As with the σ^* parameter this is due to the enthalpies' including terms involving the change of the geometry of the ring, but a relation with frequencies might well be found in the special cases of π-complexes in which no such reorganisation occurs. Reactions of olefins with silver ions, for several of which Traynham and Sehnert [14] measured the equilibrium constants, are of this type. Their values (K_e) are plotted in Fig. 3 against the corresponding C=C frequencies (for *A*, *bicyclo*[2 : 2 : 1]heptene; *B*, *cyclo*pentene; *C*, *bicyclo*[2 : 2 : 2]-octene; *D*, *cyclo*heptene; *E*, *cyclo*hexene) given by Lord and Walker.[13] Although only a few points are available a relation of the type expected appears to exist, but it is not a useful one for open-chain systems because the silver ion is known to form a complex as an hydroxylated ion [15] so that steric effects from nearby methyl groups can be considerable. The curve is however of interest from another point of view. Lord and Walker [13] showed that the effect of fusing one ring to an unsaturated one was to increase the strain as judged by the C=C frequency, which fell to a value close to that of the next smaller ring size. A fused *cyclo*pentene system for example absorbs close to *cyclo*butene. It is therefore satisfying to find that K_e for *bicyclo*[2 : 2 : 2]oct-2-ene is not the same as that of *cyclo*hexene but corresponds instead to that of *cyclo*pentene. Similarly, K_e of *bicyclo*[2 : 2 : 1]heptene is much higher than that of *cyclo*pentene and corresponds to the level of activity which might be expected from *cyclo*butene.

Conclusions.—The relations outlined support the view that frequency shifts of carefully selected vibrations can provide quantitative data on the polar properties of substituents. In general these measurements should parallel similar data from reactivities provided the latter do not relate to reactions involving electromeric effects; such comparison might be used to establish when such effects are taking place. The impact of steric effects on frequency shifts and reactivity is also noteworthy. The shifts measure the polarity or triple-bond character in the ground state, and in cyclic systems reflect the degree of strain in the bond itself (they have indeed been so used to assess relative strains in steroid systems [16]). They will be little influenced by steric effects except insofar as the latter changes bond character. But reactivities will clearly be appreciably influenced by steric factors, and the differences may lead to a useful measure of the magnitude of steric factors.

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WALTHAM ABBEY, ESSEX. [*Received, February 6th*, 1958.]

[13] Lord and Walker, *ibid.*, 1954, **76**, 2518.
[14] Traynham and Sehnert, *ibid.*, 1956, **78**, 4024.
[15] Winstein and Lucas, *ibid.*, 1938, **60**, 836.
[16] Henbest, Meakins, and Wood, *J.*, 1954, 800.

503. *Chemical Action of Ionising Radiations in Solution. Part XXII.* The Radiation Chemistry of Arsenite Solutions : the Action of X-Rays (200 kv) on Aqueous Solutions of Arsenite.*

By M. Daniels and J. Weiss.

The action of 200 kv *X*-rays on dilute aerated aqueous solutions of arsenite has been investigated over a wide range of pH. Arsenate is the only product in alkaline solution, but hydrogen peroxide is also formed in acid solution. A mechanism is proposed to account for the initial yields in acid solution, for the variation of initial yields with pH, and for the dependence of the yield on radiation dose.

Fricke and Hart [1] showed that *X*-irradiation of arsenite in the presence of oxygen afforded arsenate, and Schwarz, Losee, and Allen [2] determined the hydrogen yield (at one concentration and pH) in the absence of oxygen, using ^{60}Co γ-rays. The more extensive work of Haissinsky and Lefort [3] with α-particles and 50 kv *X*-rays appeared to produce a variety of unusual effects, in partial explanation of which reduction of arsenate by hydroxyl radicals was presumed.

This system allows wide variations of pH and it was decided to carry out a more detailed investigation using 200 kv *X*-rays.

Results

The major products of the irradiation were hydrogen peroxide and arsenate; the formation of these products, as a function of dose, in air-saturated 10^{-3}M-arsenite was investigated at pH 1·4, 8·2, and 12·7 with the results shown in Figs. 1, 2*a*, 2*b*, and 3.

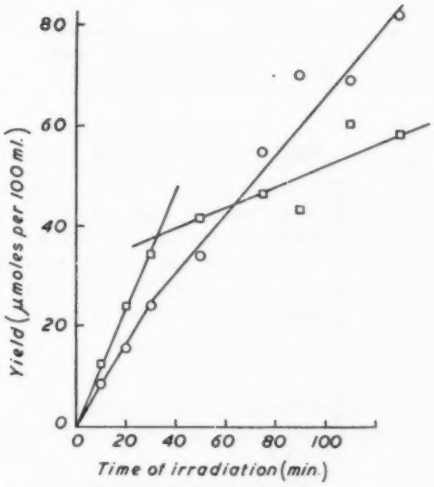

Fig. 1. *Irradiation of arsenite solutions* (10^{-3}M) *at* pH 1·4, *with* X-*rays* (200 kv). *Dose rate* = $3·2 \times 10^{-7}$ mole ev ml.$^{-1}$ min.$^{-1}$.

Yield dose dependence for the formation of arsenate (○) *and hydrogen peroxide* (□).

At pH 1·4 the initial rate of formation of As^V is linear with dose; the initial linear rate of formation of hydrogen peroxide clearly exceeds that of As^V, but a " break point," attributable to oxygen depletion, is found (Fig. 1).

At pH 8·0, whilst both rates of formation are initially linear, oxygen depletion leads to a pronounced consumption of peroxide and an increase in the rate of formation of As^V, until

* Part XXI, *J.*, 1958, 2175.

[1] Fricke and Hart, *J. Chem. Phys.*, 1936, **3**, 596.
[2] Schwarz, Losee, and Allen, *J. Amer. Chem. Soc.*, 1954, **76**, 4693.
[3] Haissinsky and Lefort, *J. Chim. phys.*, 1951, **48**, 429.

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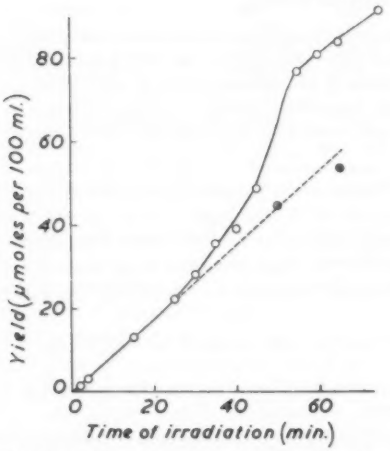
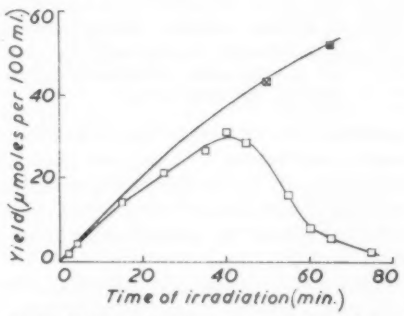
all the peroxide has disappeared (Fig. 2*a* and *b*). In solutions saturated with oxygen (1 atm.) the behaviour is comparatively simple (Figs. 2*a* and *b*).

At pH 12·7, in aerated solutions, the rate of arsenate formation is initially linear and

FIG. 2. *Irradiation of arsenite solutions* (10^{-3}M) *at* pH 8·0, *with* X-*rays* (200 kv). *Dose rate* = 3×10^{-7} mole ev ml.$^{-1}$ min.$^{-1}$.

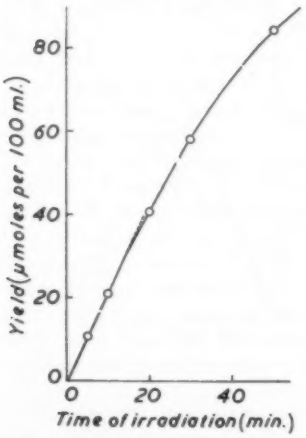


(a) *Yield–dose dependence for the formation of arsenate in air-equilibrated solution* (○) *and in* O_2 (1 *atm.*) (⊗).



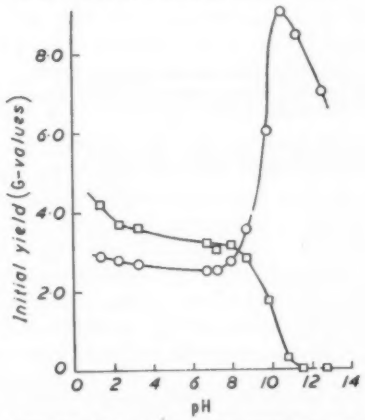
(b) *Yield–dose dependence for the formation of hydrogen peroxide in air-equilibrated solution* (□) *and in* O_2 (1 *atm.*) (⊠).

FIG. 3. *Irradiation of arsenite solutions* (10^{-3}M) *at* pH 12·8 *with* X-*rays* (200 kv). *Dose rate* = 3×10^{-7} mole ev ml.$^{-1}$ min.$^{-1}$.



Yield–dose dependence for the formation of arsenate (○).

FIG. 4. *Irradiation of arsenite solutions* (10^{-3}M) *with* X-*rays* (200 kv). *Dependence of the initial yields on* pH. *Dose rate* = 3×10^{-7} mole ev ml.$^{-1}$ min.$^{-1}$.



Arsenate (○). Hydrogen peroxide (□).

considerably greater than at lower pH; no hydrogen peroxide can be detected at this pH (Fig. 3).

In view of the large variation in the yields of As^V and the initial absence of peroxide in alkaline solutions, the dependence of the initial rates of formation of peroxide and As^V on pH was investigated in greater detail, with the results shown in Fig. 4. Here the noticeable

features are: in acid solution a continuous small decrease in the yields of peroxide and As^V with pH until neutrality is reached; and in alkaline solution a large increase in the yields of As^V and a decrease in those of peroxide, both effects reaching their maximum at pH 11; thereafter, peroxide as well as As^V contents decrease rapidly.

Discussion

Arsenious acid and arsenic acid are here represented for simplicity as H_3AsO_3 and H_3AsO_4, often abbreviated as As^{III} and As^V respectively; complications such as complex formation (*e.g.*, meta-arsenites, etc.) and degree of hydration have little effect on the argument. The conversion, $As^{III} \longrightarrow As^V$, involves the consumption of two oxidising equivalents. If it occurs in stages by single-electron transfers, it is necessary to assume the existence of an unstable intermediate of quadrivalent arsenic having some structure such as $(HO)_3As^+$; this intermediate will be represented as As^{IV}. The ultimate step in the formation of arsenate may be a reaction such as the dismutation, $2As^{IV} \longrightarrow As^{III} + As^V$.

The radiation-chemical aspect will be discussed in terms of H, OH, H_2O_2, and H_2, as the " primary products," the yields per 100 ev being designated $G(H)$, $G(OH)$, $G_M(H_2O_2)$, and $G_M(H_2)$. The measured product yields will be designated as $G(As^V)$, $G(H_2O_2)$, etc.

Our results can then be reasonably accounted for, although the overall values of G(primary products) so derived appear, in general, to vary with the solute concentration.

(i) In the presence of dissolved oxygen the reaction:

$$H + O_2 \longrightarrow HO_2 \quad \ldots\ldots\ldots\ldots (1)$$

does, under normal conditions, compete effectively for the hydrogen atoms. The situation presented in Fig. 1 then requires the following scheme of reactions to account for the high yields of peroxide and As^V:

$$OH + As^{III} \longrightarrow As^{IV} + OH^- \quad \ldots\ldots\ldots\ldots (2)$$

$$HO_2 + As^{III} \longrightarrow As^{IV} + HO_2^- \quad \ldots\ldots\ldots\ldots (3)$$

$$2As^{IV} \longrightarrow As^{III} + H_2O + As^V \quad \ldots\ldots\ldots\ldots (4)$$

$$HO_2^- + H^+ \rightleftharpoons H_2O_2 \quad \ldots\ldots\ldots\ldots (5)$$

From this, $G(As^V) = \frac{1}{2}[G(OH) + G(H)]$, and $G(H_2O_2) = G(H) + G_M(H_2O_2)$, and the higher yield of peroxide is attributable to the contribution from the " molecular yield " and because, in general, $G(H) > G(OH)$. The importance of oxygen is shown by the " break point " (Fig. 1). Although there is some scatter in the yields after this point, the most important change is in the rate of formation of hydrogen peroxide, which decreases considerably, while for arsenate the change is quite small. After the " break point," hydrogen peroxide is still being formed, in amounts comparable to the molecular yield. It seems, therefore, that the reaction:

$$H + H_2O_2 \longrightarrow H_2O + OH \quad \ldots\ldots\ldots\ldots (6)$$

cannot be taking place under these conditions. From the net rate of oxidation of arsenite after the " break point," it appears that not only OH but also H_2^+ act as oxidising species; the latter could react as follows:

$$As^{III} + H_2^+ \longrightarrow As^{IV} + H_2 \quad \ldots\ldots\ldots\ldots (7)$$

(ii) At pH 8·0, there is initially the same behaviour as at the lower pH's, *i.e.*, eqns. (1)—(5) appear to be adequate, although at this pH, the equilibrium:

$$HO_2 \rightleftharpoons H^+ + O_2^- \quad \ldots\ldots\ldots\ldots (8)$$

is practically completely shifted so as to give O_2^-, a reducing entity. However, it must be concluded that, as no marked decrease in the yields occurs, most of the radicals derived from hydrogen atoms still react according to equation (3). When oxygen consumption is complete, attack on the peroxide develops [presumably according to reaction (6)] with

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concurrent oxidation of the arsenite. Further, the peroxide consumed and the resulting " excess " of arsenate formed are roughly equivalent.

When the peroxide is completely consumed, the rate of formation of As^V decreases again, possibly owing to the back-reaction:

$$H + As^V \longrightarrow H^+ + As^{IV} \quad \ldots\ldots\ldots\ldots (9)$$

(iii) At pH 12·7, no hydrogen peroxide is found at all and the rate of As^V formation is initially linear with dose, with only slight deviations at high conversions (Fig. 3). It is known that the reaction between hydrogen peroxide and arsenite is very rapid in alkaline solution;[4] this reaction is also quantitative and may contribute to the measured yield of arsenate.

The basic problem of the effect of pH is to determine whether it can be ascribed to ionisation of solutes or to some influence on the yields of the " primary products." [5] As regards the formation of As^V and hydrogen peroxide it may be considered in two parts.

(*a*) In the region pH 7—1 there is a steady increase in $G(As^V)$ from 2·5 to 2·85 and of $G(H_2O_2)$ from 3·2 to 4·2. The increase in $G(H_2O_2)$ is 0·95 which, according to the above discussion, should be a measure of the increase of $G(H)$ with decreasing pH; this is somewhat greater than values reported by Hart [6] and Gordon and Hart.[7]

On the basis of the simple mechanism proposed for the oxidation in acid solution, values of G(primary products) can be obtained, *viz.*: $G(H_2O_2) = G(H) + G_M(H_2O_2) = 4{\cdot}2$; $G(As^V) = \frac{1}{2}[G(H) + G(OH)] = 2{\cdot}9$. $G_M(H_2O_2)$ has been determined from experiments in the absence of oxygen to be 0·8, hence $G(H) \sim 3{\cdot}4$ and $G(OH) \sim 2{\cdot}4$. These values are somewhat lower than those found by Johnson and Weiss [8] who obtained $G(H) = 3{\cdot}5$ and $G(OH) = 2{\cdot}6$, derived from yields in the ferrous and the ceric system. The values given above lead to a net water decomposition of $G(-H_2O) = ca.\ 3{\cdot}8$.

(*b*) The pH range 8—13 shows further changes in the mechanism of oxidation. The rate of peroxide production decreases to zero while $G(As^V)$ increases rapidly. There are two salient features here: first, this behaviour occurs in the pH region in which arsenious acid ionises:

$$H_3AsO_3 \longrightarrow H^+ + H_2AsO_3^-; \quad pK = 9{\cdot}22 \quad \ldots\ldots\ldots (10)$$

secondly, the increase in oxidation of the arsenite is much more than equivalent to the peroxide disappearing. Hydrogen peroxide, if formed, reacts very rapidly with arsenite at this pH:

$$H_2AsO_3^- + H_2O_2 \longrightarrow H_3AsO_4 + OH^- \quad \ldots\ldots\ldots (11)$$

However, the oxidation (11) can account only for half the arsenite formed. The rapid formation of As^V indicates a short chain-reaction and it is suggested that this is initiated by reaction of hydroxyl radicals with arsenite anions:

$$H_2AsO_3^- + OH \longrightarrow OH^- + H_2AsO_3 \quad \ldots\ldots\ldots (12)$$

which gives the intermediate As^{IV}, reaction of which with oxygen could possibly give a chain reaction of the type:

$$R + O_2 \longrightarrow RO_2 \quad \ldots\ldots\ldots (13)$$

$$RO_2 + RH_2 \longrightarrow RO_2H + R \quad \ldots\ldots\ldots (14)$$

$$RH + RO_2H \longrightarrow 2ROH \quad \ldots\ldots\ldots (15)$$

where $RH = As(OH)_3$, $ROH = AsO(OH)_3$, $RO_2 = AsO(OH)_2O_2^{\bullet}$, and $RO_2H = AsO(OH)_2O_2H$. This chain reaction could be terminated by reaction (4) or (16):

$$O_2^- + As^{IV} \longrightarrow O_2 + As^{III} \quad \ldots\ldots\ldots (16)$$

[4] Jamieson, *Amer. J. Sci.*, 1917, **44**, 150.
[5] Weiss, *Experientia*, 1956, **12**, 280.
[6] Hart, *J. Amer. Chem. Soc.*, 1955, **76**, 4198.
[7] Gordon and Hart, *ibid.*, 1955, **77**, 3981.
[8] Johnson and Weiss, *Proc. Roy. Soc.*, 1957, *A*, **240**, 189.

The rapid increase in $G(As^V)$, attributed to a chain reaction, is halted at about pH 11. There the second ionisation of arsenious acid becomes significant, but as the ion $HAsO_3^{2-}$ is even more reactive than $H_2AsO_3^-$ (*e.g.*, autoxidation occurs above pH 12) this is unlikely to decrease $G(As^V)$. The most feasible possibility is that ionisation of the hydroxyl radical:

$$OH^- + OH \longrightarrow H_2O + O^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

converts the oxidising hydroxyl radical into the reducing O^- ion, considerably decreasing the number of chain initiators. Hart, Gordon, and Hutchinson,[9] in work on radiation-induced ^{18}O exchange, give indications that effects due to such an ionisation can occur and estimate $pK \sim 9{\cdot}0$ for reaction (17). This would thus satisfactorily account for the behaviour observed.

Experimental

Materials.—Arsenite solutions (0·1N) were prepared by dissolving the weighed amount (2·473 g.) of arsenious oxide (" AnalaR ") in triply-distilled water (50 ml.) containing sodium hydroxide (" AnalaR "; 6 g.). The solution was diluted to 100 ml. and neutralised with 5 ml. of syrupy phosphoric acid as soon as possible, to avoid autoxidation (4). When the solution was to be analysed by the molybdate method (see below), neutralisation was carried out with sulphuric acid (" AnalaR "). 10^{-3}M-Solutions were prepared from this stock solution by dilution with triply-distilled water and the pH simultaneously adjusted by addition of dilute sulphuric acid or sodium hydroxide solution. In agreement with Reinders and Vles's reports [10] it was found that autoxidation of the neutralised stock solution was negligible during 3 weeks.

pH measurements were carried out with a glass-electrode system.

Radiation Procedure.—Irradiations were carried out with 200 kv *X*-rays at 15 milliamp. in an apparatus previously described,[11] on 100 ml. samples saturated with either air or oxygen. Dosimetry was carried out with ferrous sulphate in 0·8N-sulphuric acid, $G(Fe^{3+}) = 15{\cdot}6$ being used [11] and the dose rate being $3{\cdot}01 \times 10^{-7}$ mole ev ml.$^{-1}$ min.$^{-1}$.

Analysis.—Irradiation in acid solution produced hydrogen peroxide and arsenate; in alkaline solution only arsenate was found. These products were determined as follows. The hydrogen peroxide was determined colorimetrically by Eisenberg's pertitanic acid method.[12]

Arsenate was determined by two procedures: The first was a titrimetric method based on Gleu's work.[13] The initial arsenite concentration was determined by addition of the sample (5 ml.) to excess of ceric ammonium sulphate solution, 2 drops of osmic acid being used as catalyst. The excess of ceric salt was back-titrated against ferrous sulphate with *o*-phenanthroline as indicator. For the irradiated solution, the mixed solutions (ceric salt and irradiated solution) were set aside for 5 min., to permit the hydrogen peroxide to react. The osmic acid catalyst was then added and another 5 min. allowed before the excess of ceric ion was determined. By allowing for the previously determined hydrogen peroxide present in solution, the arsenate formed on irradiation could be obtained.

Being a titration procedure, the above could be used only for (relatively) large yields, and being a difference method it was liable to the accumulation of errors from the hydrogen peroxide determination. Accordingly, another method was developed, based on the formation of arseno(v)molybdate and its reduction to molybdenum-blue (see ref. 14). Hydrogen peroxide did not interfere. Agreement was found between the two methods, which are complementary; the molybdate method was used to determine initial rates of oxidation (*i.e.*, small conversions at low total dose), the ceric method for large doses which give inconveniently high optical densities in the molybdate method.

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University of Durham, King's College,
Newcastle upon Tyne, 1. [*Received, November 11th*, 1957.]

[9] Hart, Gordon, and Hutchinson, *J. Amer. Chem. Soc.*, 1953, **75**, 6165.
[10] Reinders and Vles, *Rec. Trav. chim.*, 1952, **44**, 1, 30, 249.
[11] Farmer, Stein, and Weiss, *J.*, 1949, 3241.
[12] Eisenberg, *Ind. Eng. Chem. Anal.*, 1943, **15**, 327.
[13] Gleu, *Z. analyt. Chem.*, 1933, **95**, 305.
[14] Daniels, *Analyst*, 1957, **82**, 133.

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504. *The Oxides of Uranium. Part IX.* The Decomposition of Carbon Monoxide on Uranium and Thorium Dioxides.*

By L. E. J. Roberts, A. J. Walter, and V. J. Wheeler.

The decomposition of carbon monoxide, yielding carbon and carbon dioxide, takes place much faster on urania than on thoria at 500—900°. Carbon is deposited on urania up to a limit which depends on the surface area of the urania but not on temperature. The chemisorptive capacity of urania for oxygen is decreased and oxygen is lost from the solid oxide as carbon is deposited. The addition of a little carbon dioxide to the carbon monoxide is sufficient to inhibit the decomposition; carbon dioxide is chemisorbed on urania below 200°.

Carbon monoxide decomposes rapidly at 500° on iron, nickel, and cobalt catalysts; the product consists largely of free carbon if the gas contains some carbon dioxide, and carbon deposition is negligible above 750°.[1] Bankloh and Henke reported that urania did not catalyse the decomposition of carbon monoxide,[2] and this was apparently confirmed by results reported earlier in this series.[3,4] Carbon monoxide was used at 450—750° to reduce urania to the stoicheiometric composition, without any evidence of contamination by carbon being found. Urania which was reduced in carbon monoxide showed the same chemisorption and oxidation behaviour as urania reduced in hydrogen and one sample that had been prepared by reduction of a higher oxide with carbon monoxide had a very low carbon content (<0·03 mg./g.).

Edgington and McConnell found that the chemisorptive capacity of urania for oxygen decreased after exposure to a stream of very pure carbon monoxide at 1 atm. pressure for up to 50 hours.[5] Their specimens contained appreciable quantities of carbon. We have studied the deposition of carbon on urania and both confirmed and extended their work on the effects of this carbon on the surface properties and reactivity of the urania: carbon is not deposited on urania under the conditions of reduction with carbon monoxide, normally used in the earlier researches, in which the gas in contact with the solid contained a little carbon dioxide. A few experiments were carried out on thoria.

Experimental

Flow Experiments.—Carbon monoxide from a cylinder was passed through a liquid-oxygen trap, copper gauze at 500°, and another liquid-oxygen trap, and led over weighed specimens of oxide (1—2 g.) in silica U-tubes at about 100 c.c./min. Two or three silica U-tubes were sometimes placed in series, each in a separate furnace; two or three specimens could thus be exposed to the gas stream for different times. A reduction treatment preceded each run; the urania was treated with a static atmosphere of 30 cm. of carbon monoxide for 30 min. at 500°, or with 10—15 cm. of hydrogen for 30 min. at 600°, followed by pumping at 650—750°.

The carbon deposited on the oxide was estimated by heating it in a slow flow of oxygen at 750°, collecting the carbon dioxide in a trap at −183°, and measuring its volume with the

* Part VIII, *J.*, 1957, 3679.

Erratum.—The factor π^2 was erroneously omitted from the exponent in the diffusion equation quoted as eqn. (3) by Anderson and Alberman (*J.*, 1949, S303) and as eqn. (2) by Anderson, Roberts, and Harper (*J.*, 1955, 3946). The equation should read

$$\frac{\bar{C}}{C_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-n^2\pi^2\frac{Dt}{a^2}\right).$$

This was the equation actually used in the calculations and the numerical values of D quoted need no correction. We thank Dr. E. A. Gulbransen for bringing this to our notice.

[1] Taylor, *J. Iron Steel Inst.*, 1956, **184**, 1.
[2] Bankloh and Henke, *Metallwirtschaft*, 1940, **19**, 463.
[3] Roberts, *J.*, 1955, 3939.
[4] Anderson, Roberts, and Harper, *ibid.*, p. 3946.
[5] Edgington and McConnell, unpublished work, A.E.R.E., Harwell.

trap at −80°; any water formed could subsequently be measured with the trap at room temperature.

Circulating-gas Experiments.—For apparatus, see Fig. 1. The all-glass pump was based on an earlier design [6] further developed in these laboratories by P. C. Davidge. An iron rod was sealed between springs inside a glass piston which was a sliding fit inside a " Veridia " tube of accurate dimensions. The barrel was mounted vertically and the piston was moved by supplying direct current alternately to two solenoids. A system of glass valves made the gas flow unidirectional, and rates of 200 c.c./min. were easily obtained.

The gas passed over the oxide in a U-tube, and then through a trap which could be cooled. The volumes of all parts of the apparatus were determined by comparison with a standard volume, so the quantity of gas in the system could be calculated after measurement of the pressure on the constant-volume manometer. The trap could be evacuated independently of the main apparatus, and its contents measured after warming to −80° or room temperature.

The urania specimens were reduced at the start of each experiment by circulating carbon monoxide at 500°, with the trap at −183°. The reduction was orders of magnitude faster than the rate of carbon deposition at 500°, and at the end of the reduction stage the pressure of the carbon monoxide became approximately constant. Reduction took less than 30 min. at 500°. Carbon deposition was studied by measuring out a volume of carbon monoxide and circulating it for a known time with the oxide specimen at a given temperature. In some

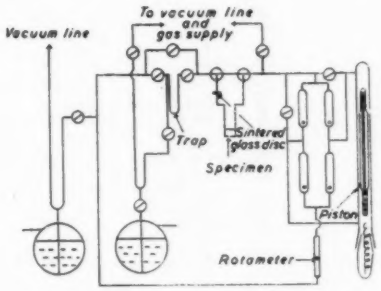

FIG. 1. *Apparatus used for circulating-gas experiments.*

experiments, the carbon dioxide was continuously removed from the gas stream by cooling the trap with liquid oxygen, and the amount formed estimated from time to time by isolating the trap, evacuating, and warming. In other experiments, the carbon dioxide was not continuously removed, but was collected at the end of an experiment by evacuating the circulating system through the cooled trap. A technique that removed more than 99% of the carbon dioxide from the gas was to circulate for 10 min. with the trap at −183°, and finally to evacuate slowly through the trap, the evacuation being controlled with a stopcock so that the gas flowed through the trap at low pressure.

The carbon in an oxide specimen was determined by circulating pure oxygen over the hot oxide, with the trap cold, until the pressure became constant, and measuring the carbon dioxide produced.

Adsorption and Oxidation Experiments.—The adsorption and oxidation characteristics of some urania samples were determined after carbon deposition without exposure to air. Chemisorption of oxygen at −183° was determined as the difference between two adsorption isotherms at −183° which were measured before and after pumping at −80°; [7] the second isotherm was assumed to represent physical adsorption and was analysed by the B.E.T. equation to give a value of V_m, the volume of gas in c.c. at N.T.P. in a physically adsorbed monolayer of oxygen at −183°.

The rates of reaction with oxygen at 18° and subsequently at 142° were determined in a constant-volume apparatus by measuring the rate of fall of pressure, again without exposure of the urania to air after depositing carbon.

Materials.—Two samples of urania were used, both prepared from U_3O_8 which had been made from the pure grade of " ammonium diuranate " available in this Establishment. One

[6] Brenschede, *Z. phys. Chem.*, 1936, **178**, 74.
[7] Roberts, *J.*, 1954, 3332.

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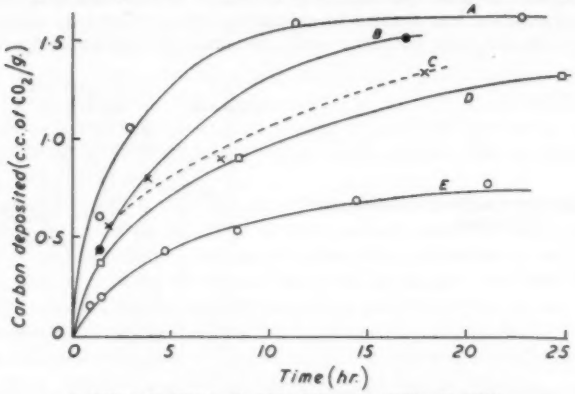
sample (C3) had been prepared by reduction with carbon monoxide at 700°, and the other (C4) by reduction with hydrogen at 760°. The characteristics of these preparations respectively were: density, 10·90, 10·76 g./c.c.; mean particle size, 0·41, 0·47 micron; mean crystallite size, 0·38, 0·53 micron. Probably most of the particles were single crystals.[8]

Two samples of thoria were prepared by heating a pure grade obtained from Thorium Ltd. to about 1000° in air.

Results

Rate of Reaction.—The amount of carbon deposited on urania is plotted against time of exposure to carbon monoxide at various temperatures and pressures in Figs. 2 and 3; the carbon content is expressed as the volume (c.c. at N.T.P./g.) of carbon dioxide produced upon subsequent oxidation. The results at 1·1 atm. pressure (Fig. 2) are those of flow experiments; pre-reduction was usually carried out with hydrogen and the carbon was directly determined; a fresh oxide sample was used for each run. Specimen C4 was used for all experiments except one series (broken curve) at 500° on C3. The flow rate was about 100 c.c./min.; markedly

Fig. 2. *Deposition of carbon on urania from carbon monoxide at* 1·1 *atm. pressure.*



A, 750°; *B*, 700°; *C*, 500° (C3); *D*, 650°; *E*, 500°.

less carbon was deposited when the flow rate was reduced to about 20 c.c./min. Results at lower pressures (Fig. 3) were obtained both in flow and in circulation experiments. Specimen C4 was used throughout and the flow experiments were conducted exactly as at 1·1 atm.

The gas-circulating experiments to determine reaction rates were conducted with continuous removal of the carbon dioxide from the gas stream and the variation of gas pressure with time was recorded. The calculation of the amount of carbon deposited was made by assuming that the ratio (CO_2 produced : CO lost) for any stage in the reaction was that determined in other experiments (see below) at the same temperature. Then, by material balance,

$$\text{Carbon deposited} = (\text{CO lost}) - (\text{CO}_2 \text{ produced}) \text{ for that time interval}$$

The errors in such a procedure are cumulative and tend to be large because the amount of carbon monoxide lost was less than 10% of the total amount in the system. The figures for carbon deposited in any time interval were therefore corrected by multiplying by the ratio (C found : C calculated), where "C found" is the carbon determined by analysis at the end of the run and "C calculated" is the sum of the amounts of carbon deposited in the various time-intervals, as calculated from the amount of carbon monoxide lost. Two or three such experiments were carried out at each temperature; the results were in fair agreement and averaged values are plotted in Fig. 3. The results were compatible with those of the flow experiments and good agreement was directly established at 700° and 0·45 atm.

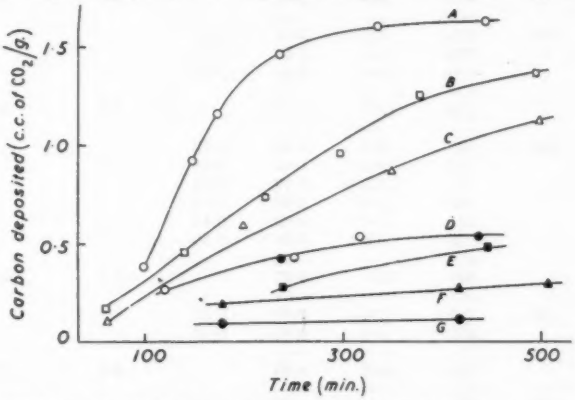
The rate of deposition of carbon increased regularly with both pressure and temperature. Comparison of the initial rates of reaction at 750°, 700°, and 650° shows that the rate is more

[8] Anderson, Harper, Moorbath, and Roberts, A.E.R.E. C/R 886.

nearly proportional to the first power of the pressure than to any other simple-power law and this is also found to be so when the rates at different pressures at 750° are compared at times of equal carbon deposition. The reaction becomes so slow below 650° and below 1 atm. that no firm statement can be made. At any one pressure, the rate increases regularly with temperature and there is no sign that the rate reaches a maximum in the temperature range studied. The form of the kinetic curve was always that of a reaction proceeding to a definite limit and the maximum amount of carbon deposited seemed to be independent of the rate of deposition. The maximum amounts of carbon deposited in different long runs were: C4: 900°, 0·45 atm., 1·61 and 1·62 c.c. CO_2/g.; 750°, 1·1 atm., 1·62 c.c./g.; 790°, 0·45 atm., 1·84 c.c./g.; C3: 900°, 0·45 atm., 1·89 c.c./g.

The rate of deposition of carbon at 500° was faster on specimen C3 than on C4 (Fig. 2), in accordance with the larger surface area of C3. The rate of deposition on the same area of

FIG. 3. *Deposition of carbon on urania from carbon monoxide at low pressures.*



Open symbols: circulating-gas experiments; full symbols: flow experiments.
A, 900°, 0·45 atm.; *B*, 800°, 0·45 atm.; *C*, 750°, 0·45 atm.; *D*, 700°, 0·45 atm.; *E*, 650°, 0·64 atm.; *F*, 650°, 0·31 atm.; *G*, 500°, 0·31 atm.

thoria was much lower. The results on two specimens of thoria are in Table 1, together with the values of V_m; the amount of carbon deposited is expressed as c.c. of CO_2 collected on analysis. The ratio (volume of CO_2 collected) : V_m (Table 1), which is a measure of the carbon deposited per unit surface area, can be compared with the values for urania C4, for the same temperature, pressure, and duration of experiment, in the last column; the reaction proceeded 3—7 times faster on urania than on the same area of thoria.

TABLE 1. *Decomposition of carbon monoxide on thoria.*

Oxide	V_m (c.c./g.)	Conditions	Time (min.)	Temp.	c.c. of CO_2/g.	c.c. of CO_2/g. / V_m	c.c. of CO_2/g. of UO_3 / V_m
Th/0	0·90	Flow, 1·1 atm.	180	505°	0·03	0·033	1·0
		,,	180	650	0·21	0·23	1·8
		,,	360	650	0·46	0·51	2·5
		,,	180	745	0·65	0·73	3·2
Th/1	0·50	Circulating, 0·4 atm.	320	850	0·40	0·80	3·8

Stoicheiometry of the Reaction.—The results of experiments in the gas-circulating apparatus in which the carbon dioxide was continuously removed from the gas stream are collected in Table 2. The calculated value for the carbon deposited, expressed as before as c.c. of CO_2, is the difference between the total volumes of carbon monoxide lost and carbon dioxide formed. The actual amounts of carbon found by analysis after each experiment are given in column 9; the results in parentheses were obtained after the circulation of CO–CO_2 mixtures under

conditions in which it is unlikely that carbon is either deposited or removed (see below). The agreement between the calculated and observed values for carbon is reasonable in view of the likely errors in the measurement of volumes of carbon monoxide; the total amount of carbon monoxide was in all cases about 100 c.c. at N.T.P. at 0·4—0·45 atm. The errors in two runs (C4/9 and C4/21) were noticeably higher than the average.

TABLE 2. *Gas-circulating experiments with trap at* −183°.

Run	Weight (g.)	Temp.	Time (min.)	CO lost (c.c., N.T.P.)	CO_2 found (c.c., N.T.P.)	CO_2/CO	Carbon calculated (c.c. of CO_2)	Carbon found (c.c. of CO_2)	Oxygen lost (c.c./g.)
C4/9	3·702	650°	172	1·4	0·73	0·52			
			350	2·1	0·84	0·40			
			330	2·0	0·90	0·45			
			852	5·5	2·47		3·0	1·33	0·16
C4/8	3·644	750	175	5·5	3·31	0·60			
			175	2·4	1·40	0·58			
			420	4·9	2·45	0·50			
			770	12·8	7·16		5·6	5·36	0·25
C4/10	3·464	800	66	2·1	1·53	0·73			
			95	2·8	1·84	0·66			
			75	2·5	1·17	0·47			
			88	2·2	1·14	0·52			
			141	1·8	0·89	0·49			
			175	0·6	0·30	0·50			
			640	12·0	6·87		5·1	5·34	0·22
C4/4	3·461	790	290	7·4	4·03	0·55			
			435	8·4	4·83	0·58			
			725	15·8	8·86		6·9	(6·37)	0·36
C4/21	3·543	900	38	1·4	1·51	1·08			
			80	3·0	1·92	0·64			
			85	4·3	2·14	0·50			
			215	3·3	2·00	0·61			
			418	12·0	7·57		4·4	(5·74)	0·26
C4/18	3·457	900	450	12·2	7·10	0·58	5·1	(5·57)	0·22
C4/2	4·769	750	520	13·1	7·10	0·54	6·0	5·07	0·21
C4/14	4·051	700	345	5·4	3·19	0·59	2·2	—	—
Th1/2	5·926	850	320	—	4·23	—	—	2·38	0·155

In every case except one (C4/9), the volume of carbon dioxide collected was greater than half the volume of carbon monoxide lost, and the decomposition cannot be represented simply by the formula $2CO \longrightarrow C + CO_2$. Extra oxygen must have been obtained from the oxide. The amount can be estimated from the difference between the volume of carbon dioxide collected during the experiment and the volume obtained on analysis for carbon; both these volumes were comparatively small and were accurately measured. Half this difference is the volume of oxygen lost from the oxide, listed in the last column of Table 2. The low value for the volume of carbon monoxide lost recorded for run C4/9 is clearly due to the difficulty of measuring accurately such small changes in the volume of carbon monoxide.

The results of experiments in which carbon dioxide was not removed from the gas stream are in Table 3. The original composition of the gas is given in columns 4 and 5, and the carbon dioxide content of the gas at the end of the run in column 8. The total pressure of gas was in all cases 0·4—0·5 atm. The carbon on the oxide is given in column 3; the second figure listed for each run is the carbon determined by analysis at the end of the experiment, and is accurate, while the first is the carbon estimated to be present at the start of the experiment from the results of a previous deposition run, and is liable to considerable error for the reasons already

discussed. The amount of oxygen lost from the solid, calculated as before, is recorded where possible in the last column.

TABLE 3. *Gas-circulating experiments with trap at room temperature.*

Run	Weight (g.)	Carbon on oxide (c.c. of CO_2)	Original gas CO (c.c.)	Original gas CO_2 (c.c.)	Temp.	Time (min.)	Final gas CO_2 (c.c.)	Oxygen lost (c.c./g.)
C4/11	3·886	0	117	0	800°	330	0·92	
			135	0	,,	250	1·62	
			116	0	,,	108	0·62	
			125	0	,,	180	1·01	
			121	0	,,	150	0·67	
		3·72				1018	4·84	0·15
C4/13	3·767	0	110	0	800	780	0·74	
			109	0·74	,,	240	0·76	
		0·26				1020	0·76	0·067
C4/3	3·244	0	106	0	730	310	0·92	
			140	0	,,	288	0·78	
		0·087				598	1·70	0·24
C4/19	3·759	0	90	2·60	800	270	2·91	
		0·03						0·040
C4/14	4·051	(2·2)	116	0	750	405	0·58	
			123	0·54	,,	320	1·03	
			121	1·03	,,	210	1·13	
		3·69	133	0	,,	235	0·43	
C4/6	3·013	(4·3)	110	0	740	335	0·04	
			94	4·12	,,	416	4·32	
		3·8	100	4·32	,,	206	3·95	
C4/21	3·543	(4·4)	97·5	18·42	750	115	17·87	(−0·078)
			93·5	17·87	,,	100	17·81	
		5·74	86·7	17·81	,,	122	17·84	
C4/23	5·781	(1·3)	~100	3·57	850	60	3·14	(−0·04)
			~100	3·12	,,	270	3·11	
			~100	3·11	,,	120	3·07	
		CO circulated at 850° with trap at −183°; 2·61 c.c. of CO_2 collected.						
		3·90	100	2·61	850	90	2·23	(−0·033)
C4/17	4·481	(5·6)	0	65·9	750	278	61·9	
		2·23						
Th1/3	5·926	0	121	0	850	26	1·45	
		0·05	126	1·45	,,	125	1·48	0·118
Th1/5	5·926	0	128	3·93	850	140	5·17	0·105
		0·01						

In the first three experiments in Table 3, pure carbon monoxide was circulated over a freshly-reduced, clean specimen of oxide. The apparent rate of decomposition was far lower than it had been when the carbon dioxide formed was continuously removed, and the result of C4/13 indicated that the reaction stopped when the carbon dioxide concentration had reached a limiting value, which varied in different experiments from 0·5 to 1·2% of the total gas. Very little carbon was deposited when a larger concentration of carbon dioxide was initially added to the carbon monoxide (C4/19).

A similar result was obtained when pure carbon monoxide was circulated over an oxide holding some carbon (C4/14); carbon dioxide production continued up to a gas content of 0·93%, by which time the reaction had practically stopped, but removal of the carbon dioxide and circulation of fresh carbon monoxide led again to the production of more carbon dioxide.

Circulation of gas mixtures containing more than 4% of carbon dioxide seemed to remove little or no carbon, which would cause the carbon dioxide content of the gas to fall. This was investigated in detail by using two specimens, one of which had been " saturated " with carbon

(C4/21), while the other (C4/23) held about half this amount. Loss of carbon dioxide occurred the first time a mixture rich in carbon dioxide was circulated over these specimens, but no change occurred during subsequent runs. Circulation of pure carbon monoxide, with removal of the carbon dioxide produced, regenerated a surface that would react with a little carbon dioxide. Continuous removal of carbon was clearly not taking place. The loss of carbon dioxide during the first runs following carbon deposition is then due to oxidation of the oxide by carbon dioxide rather than to the removal of carbon; the amounts of oxygen gained by the oxide, on this assumption, are given in parentheses as a " negative loss " in the last column of Table 3.

Pure carbon dioxide did remove some carbon from a carbon-loaded oxide (C4/17); 4 c.c. of CO_2 was lost in 278 min. at 750°, and the subsequent analysis for carbon gave a figure 3·4 c.c. lower than the amount calculated to have been deposited. This amount is well outside the usual error on the calculated amount of carbon deposited.

The results of two experiments on thoria are recorded at the end of Table 3. Carbon deposition was inhibited by the presence of about 1% of carbon dioxide, though it proceeded normally if the carbon dioxide was removed, as shown by the last experiment in Table 2. The rapid production of carbon dioxide at first, associated with considerable loss of oxygen from

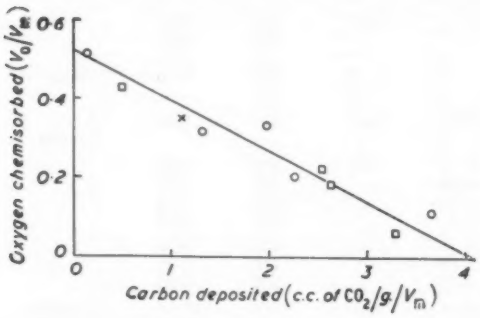


FIG. 4. *The effect of carbon deposition on urania on the chemisorption of oxygen at −183°.*

○, C3; □, C4; ×, reactive UO_2 from Edgington and McConnell.

the oxide, is due to these samples' not being given the prior reduction that the urania samples received (see p. 2480).

Reaction on Silica.—Blank runs on the empty silica container were carried out from time to time to check the purity of the carbon monoxide and the extent of the decomposition on the silica walls. Carbon monoxide was circulated for between 4 and 6 hr., with the silica at 700—850° and the trap cold. The highest amount of carbon dioxide collected was 0·11 c.c. from 121 c.c. of carbon monoxide, and the smallest amount was 0·04 c.c. from 120 c.c. of carbon monoxide. Some water was also found—about double the amount of carbon dioxide—presumably formed from hydrogen impurity in the carbon monoxide. A mixture of 2·538 c.c. of carbon dioxide and about 100 c.c. of carbon monoxide was circulated through a silica tube at 850° for 2 hr.; 2·524 c.c. of carbon dioxide was recovered at the end. The reaction with silica was therefore negligible under all conditions.

Carbon Dioxide–Urania Reaction.—The adsorption of carbon dioxide was studied with a sample of urania C4 which had been reduced with carbon monoxide as usual. A slow adsorption occurred at low temperature, 0·135 c.c./g. being adsorbed in 14 hr. at 25° and 13 cm. pressure, and 0·123 c.c./g. in 2 hr. at 100° and 13·8 cm. All the gas was recovered by heating above 200° and no adsorption could be measured at 500°, 650°, or 800°.

Oxidation might have occurred, to form carbon monoxide, without change in gas volume. To check this, 89 c.c. of carbon dioxide were circulated for 5 hr. over 3·25 g. of urania C4 at 750° after the usual reduction period. The carbon dioxide was pumped off and the degree of oxidation assessed by circulating pure carbon monoxide for 30 min. at 650°, after which 0·72 c.c. of carbon dioxide was found in the gas. The oxygen absorption by the urania from the carbon dioxide was therefore 0·11 c.c./g., and this is a maximum value, since it would have included any carbon dioxide formed in the initial stages of the usual carbon deposition process (see above).

Chemisorption and Oxidation Properties.—The results plotted in Fig. 4 illustrate the decrease

in the chemisorption of oxygen at −183° on urania that occurs as carbon is deposited. V_o/V_m is the ratio of the oxygen chemisorbed at −183° to the volume of oxygen in a physically-adsorbed monolayer, and the carbon content is expressed as c.c. of CO_2/g. divided by V_m to refer the results on different samples to the same surface area of oxide. Carbon was deposited under flow conditions at 500° in most cases and 650° in others on C3 and C4. The values of V_m varied considerably amongst themselves, those for C3 samples varying from 0·37 to 0·43 c.c./g. and for C4 from 0·30 to 0·33 c.c./g. with one of 0·41 c.c./g.; this variation is almost certainly due to the particle division which occurs when a partially-oxidised sample of urania is heated before the first reduction treatment.[4] Also plotted in Fig. 4 is one (unpublished) result obtained by Edgington and McConnell [5] on a very reactive sample of urania, having $V_m = 3·9$ c.c./g.

The rate of oxidation of C3 at higher temperatures was determined after deposition of carbon to a limiting value of 1·89 c.c. of CO_2/g. The oxidation at 4·7 cm. and 18° followed the normal logarithmic dependence on time [4] but the rate of reaction was about a quarter of that of the rate with carbon-free C3 specimens under the same conditions. The rate of oxidation at 142° and 3·5 cm. also followed the expected kinetic law,[4] and the results for the first 60 min. fitted the parabolic equation

$$V = 0·082\sqrt{t} + 0·09$$

where V is the volume of oxygen absorbed (c.c. of O_2/g.) in t min. This is again a factor of 3 or 4 slower than the rate of oxidation previously determined. Only 0·01 c.c. of carbon dioxide was found in the residual oxygen at the end of the experiment.

Discussion

The results in Tables 2 and 3 establish that oxygen is lost from urania during the deposition of carbon. The CO_2 : CO ratios listed in Table 2 are admittedly not very accurate, but the general tendency is clear: more oxygen is lost from the oxide early in the reaction than later. The results of the first experiments in Table 3 show, however, that some deposition of carbon does occur in the early stages and the amounts of oxygen lost from the oxide tend to be higher the more carbon is deposited. The two processes, oxygen loss and carbon deposition, probably occur simultaneously but not at the same rates.

The two processes are linked. The decomposition stops when the carbon dioxide content of the gas is about 1%. This is not due to an equilibrium state's being reached, in which the rates of deposition and removal of carbon are equal, since there is no evidence that carbon is removed at any appreciable speed when gas mixtures containing much more carbon dioxide are circulated over carbon deposits, and the rate of removal of carbon was very slow compared with the rate of deposition from pure carbon monoxide, even when pure carbon dioxide was used. The loss of carbon dioxide that occurs the first time a CO–CO_2 mixture is circulated over urania holding appreciable carbon is more readily explained as being due to loss of oxygen from the carbon dioxide, replacing some of the oxygen lost from the oxide during the deposition of carbon. It seems clear that it is the re-adsorption of this small amount of oxygen which inhibits the further deposition of carbon; the decomposition is then controlled by an equilibrium involving oxygen, not carbon. Re-exposure to pure carbon monoxide results in reduction of the oxide again, and more carbon can be deposited (*e.g.*, C4/23, Table 3); subsequently, oxygen can again be adsorbed from a CO–CO_2 mixture. The fact that a little oxygen is lost from urania when a gas mixture containing as much as 2·9% of carbon dioxide is circulated before any carbon has been deposited (run C4/19, Table 3) indicates that the oxygen activity is higher initially than it is after oxygen has been removed and carbon deposited; this is inherently reasonable and in line with the other evidence that oxygen is removed predominantly in the early stages of the reaction. The total oxygen loss from urania during carbon deposition reached 0·26 c.c./g. on C4, the higher value in run C4/4 (Table 2) being almost certainly due to a high surface area value for this specimen as shown by the high

value for the carbon deposited. A single layer of O^{2-} ions in the surface of a urania sample having $V_m = 0{\cdot}32$ c.c./g. would be about 0·42 c.c. of O_2/g.,[9] so that oxygen equivalent to 60% of a single layer is lost during carbon deposition. The amounts of oxygen which are sufficient to stop the reaction when re-absorbed at a later stage amount to less than 30% of the total oxygen loss.

The few results available indicate that oxygen equilibria also control the deposition of carbon on thoria. The thoria samples had no prior reduction treatment but were used after ignition in air. The comparatively large oxygen loss that rapidly occurred in carbon monoxide has been shown in other work to be entirely independent of the deposition of carbon and to comprise 10—20% of the oxygen in the thoria surface.[10] A corresponding loss of oxygen from urania would certainly have occurred during the prior reduction stage. The amount of oxygen lost from a thoria sample on which appreciable carbon had been deposited was higher than the amount that was quickly lost before carbon deposition began [cf. Th 1/2 (Table 2) with Th 1/3 and Th 1/5 (Table 3)] so that further oxygen is lost from thoria as carbon deposition proceeds.

This result is evidence that the oxygen which is removed from urania as carbon deposition occurs is not the last trace of interstitial oxygen which is not removed by the prior reduction treatment, since thoria would not be expected to contain any appreciable amount of interstitial oxygen. The abrupt change in reaction rate provided additional evidence; the prior reduction stage, involving removal of interstitial oxygen,[4] is very rapid at 600°, 1·8 c.c. of O_2/g. being removed in less than 15 min., while oxygen loss accompanying carbon deposition occurs for at least two hours at 800° and probably proceeds slowly for as long as carbon is being deposited. It seems likely that this oxygen loss is a surface, not a bulk, phenomenon.

The simplest hypothesis to explain the almost linear fall in chemisorptive capacity with carbon deposition (Fig. 4) is that the carbon is uniformly distributed over the surface. The differential heat of adsorption of oxygen at −183°, at low coverage, is not affected by the presence of some carbon on the surface,[11] so it appears that it is the number and not the nature of the adsorbing centres which is affected by carbon. The line drawn through the experimental points in Fig. 4 extrapolates to $V_o/V_m = 0{\cdot}52$ with no carbon on the surface, in good agreement with other observations that $V_o/V_m = 0{\cdot}50$—$0{\cdot}56$ for urania samples of this type.[12] Also, the chemisorption of oxygen falls to zero at a carbon content of 4·1 c.c. of CO_2/V_m which is rather less than the corresponding figures for the maximum carbon deposition on urania, which are 4·7 and 4·9 c.c. of CO_2/V_m for samples C3 and C4 respectively, suggesting that deposition stops when the surface is nearly completely covered. The maximum number of surface uranium atoms per physically-adsorbed oxygen molecule is 1·3.[9] The maximum carbon deposition is thus equivalent to at least 3·8 carbon atoms per surface uranium atom, or 1·9 carbon atoms per surface oxygen atom, if the carbon is deposited evenly. This seems to be spatially possible, for the minimum diameter of a C_2 group in UC_2 is about 3·0 Å and the diameter of an O^{2-} ion in urania is about 2·7 Å.

The formation of a " surface carbide " might be possible under the conditions used even though the formation of bulk carbide is thermodynamically impossible.[13] The formation of a thin layer of carbon over the surface in this case may explain why the general features of the reaction are so different from those characteristic of the decomposition of carbon monoxide on metal catalysts, when bulk carbon can be formed.[1] The only conflicting observation is the light-grey colour of the thoria samples after carbon deposition, which would usually be taken as evidence for the formation of discrete particles

[9] McConnell and Roberts, " Chemisorption," Butterworths, London, 1957, p. 218.
[10] Roberts and Walter, unpublished work.
[11] Ferguson and McConnell, *Proc. Roy. Soc.*, 1957, *A*, **241**, 67.
[12] Roberts, *J.*, 1954, 3332.
[13] Heusler, *Z. anorg. Chem.*, 1926, **154**, 364.

of carbon or of thick, local deposits. However, it is not certain that all the deposition occurred in the same manner on the two oxides; the rate of reaction was much slower on thoria, and the thoria samples were of smaller particle size than the urania; there is other evidence for the deposition of free carbon on an " active " surface of thoria.[14]

A detailed explanation of the kinetics will not be attempted here because of the complex nature of the deposition reaction. The " autocatalytic " appearance of the early stages of the high-temperature runs (Fig. 3) may be due to a real acceleration of the carbon deposition as the oxide surface is stripped of oxygen, or it may be due to the difficulty of displacing carbon dioxide efficiently from the powder bed, which was 5 mm. thick, at high reaction rates. The kinetic curves in Fig. 2 approximate to the shape expected if the diminution in rate with time is due to the gradual occupation of a fixed number of suitable sites. The rate of deposition of carbon is approximately dependent on the first power of the pressure of carbon monoxide. This would be the case if the reaction were between carbon monoxide in the gas phase and adsorbed carbon monoxide, if adsorption equilibrium was quickly established. Adsorption of carbon monoxide on urania has been shown not to be extensive at the temperatures used here, but no results obtained now or previously rule out the possibility that carbon monoxide is quickly adsorbed on a few sites, and these might be oxygen vacancies, since the re-adsorption of as little as 8% of the oxygen in a surface layer was sufficient to stop the deposition of carbon in some cases.

ATOMIC ENERGY RESEARCH ESTABLISHMENT, HARWELL. [*Received, December 17th*, 1957.]

[14] D'Eye and Sellman, A.E.R.E. C/R 1286.

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505. *Depolarisation by Oxygen and by Hydrogen Peroxide at Graphite Cathodes in Alkaline Solutions.*

By A. A. MOUSSA, H. K. EMBABY, and H. M. SAMMOUR.

Re-examination of the equilibrium between oxygen and alkaline peroxide solutions at spectroscopically pure graphite electrodes in the form of short cylindrical rods confirms earlier results. On cathodic polarisation, the potential depends markedly on the rate of stirring of the electrolyte, and in 1·0M-sodium hydroxide vigorously stirred with oxygen the current–potential curve reveals two distinct depolarisation stages before hydrogen is evolved. The first corresponds to the almost quantitative reduction of oxygen to hydrogen peroxide, and the second to reduction of the latter. With previously heat-activated electrodes, however, the potential was independent of stirring, and the yield of peroxide was only 35—45% of theory. Some aspects of the reduction mechanisms and their analogy to those accepted to account for the phenomenon observed at the dropping-mercury cathode are discussed.

THERE is little information about the rôle of depolarisation by oxygen and hydrogen peroxide of graphite cathodes in alkaline solution. Such as there is is difficult to compare owing to the ill-defined nature of the carbons used and the widely different methods of pre-treatment and their effect on the yield of peroxide produced cathodically; also the form of electrode which would permit adequate interpretation of the results is in doubt.[1] With graphite electrodes, in the form of hollow blocks through which oxygen was forced, Berl [2] showed that the equilibrium $O_2 + H_2O + 2e \rightleftharpoons OH^- + HO_2^-$ could be readily established at purely graphite surfaces or surfaces covered with activated carbon, although

[1] Herbert, " Zur Frage des Brennstoffelementes," Diplomarbeit, Darmstadt, 1928; Skumburdis, *Kolloid Z.*, 1931, **55**, 156; E. Berl, *Trans. Electrochem. Soc.*, 1939, **76**, 359; Brushtein and Frumkin, *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 327; Shigeru and Mizuno, *Bull. Tokyo Inst. Technol.*, 1948, **13**, 102.

[2] W. G. Berl, *Trans. Electrochem. Soc.*, 1943, **83**, 253.

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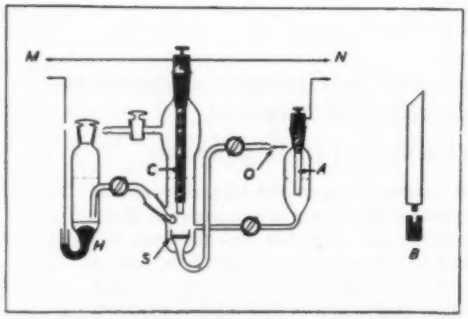
the two types of surface gave very different yields of hydrogen peroxide during cathodic polarisation; the former produced insignificant amounts and the latter almost 100% yield over a wide range of current density. Weizse and Jaffe [3] confirmed Berl's results and inferred that in both acid and alkaline air-depolarised cells hydrogen peroxide is catalytically decomposed. Regarding the mechanisms, Yeager *et al.*[4] showed that peroxide is formed on carbon electrodes in alkaline solutions rapidly and reversibly through the cathodic reduction of adsorbed oxygen, but Bratzler [5] postulated an oxonium salt-like structure as intermediate and the participation of atomic hydrogen produced by the primary discharge process. No result on the electroreduction of peroxide at graphite electrodes seems to have been published.

We used a simple spectroscopically pure graphite electrode to examine the equilibrium between oxygen and alkaline peroxide solutions, and the rôle of depolarisation by oxygen at 1 atm. and by hydrogen peroxide at different concentrations. Preliminary results about the effect of the state of the surface on the course of the reduction of oxygen and the yield of peroxide are also reported.

Experimental

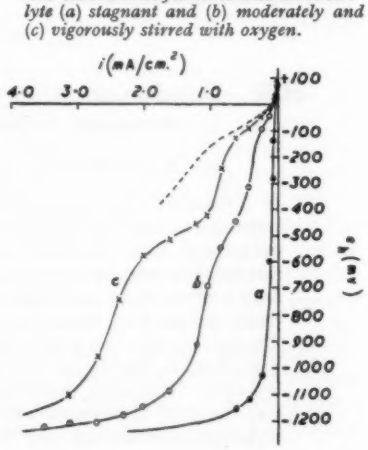
Electrodes.—Spectrographically standardised graphite (Johnson and Matthey) was used, supplied as cylindrical rods 30 cm. long and 6·5 mm. in diam. About 10 cm. lengths were protected in tightly fitting Polythene tubing except for a length of *ca.* 2 cm. left uncovered to serve as electrode. The electrodes were boiled with 4N-hydrochloric acid, rinsed with water, and then boiled with dilute sodium hydrogen carbonate solution. The surface was then left untouched, and when not in use the electrodes were kept under distilled water.

Fig. 1.



C, Cathode; *H*, saturated calomel half-cell; *A*, auxiliary graphite anode; *O*, entry for pure oxygen; *S*, sintered glass disc; *M*, *N*, connections to potentiometer and polarising circuits, respectively.

Fig. 2. *Current–potential curves obtained in* 1·0M-*sodium hydroxide with the electrolyte* (*a*) *stagnant and* (*b*) *moderately and* (*c*) *vigorously stirred with oxygen.*



Materials.—Inhibitor-free hydrogen peroxide was prepared from 40% sulphuric acid and sodium peroxide (B.D.H.).[6] The product after two distillations over silver sulphate varied in concentration from 1·0 to 3·0M and was used as a stock. Sodium hydroxide solutions were prepared by dilution of a carbonate-free concentrated solution of "AnalaR" solid. Water was twice distilled over alkaline permanganate.

[3] Weizse and Jaffe, *Trans. Eletrochem. Soc.*, 1948, **93**, 128.
[4] Yeager, Witherspoon, Urbach, Yeager, and Hovorka, Tech. Report No. 4 (Second series) to the Office of Naval Research, Washington, October 1954.
[5] Bratzler, *Z. Elektrochem.*, 1950, **54**, 81.
[6] Kilpatrick, Reiff, and Rice, *J. Amer. Chem. Soc.*, 1926, **48**, 3019.

Analysis.—Peroxide was determined colorimetrically with a Hilger absorptiometer, a 2% solution of " AnalaR " titanyl potassium oxalate in 5N-sulphuric acid being used as reagent. With 5N-sulphuric acid as diluent, use of a 1 cm. cell and a Hilger No. 1 blue filter gave a linear (±3—5%) density–concentration curve from 20 to 80 mg. $l.^{-1}$ of peroxide.

Electrical Measurements.—Polarisations were carried out in a Pyrex glass cell (Fig. 1). For open-circuit measurements the auxiliary anode side compartment was omitted. All measurements were made at 25° ± 0·1° (air thermostat). Potentials were recorded with a circuit incorporating a Ferranti electrometer valve and a Tinsley potentiometer of range 0—1·9 v. Polarisation current was supplied by a dry battery and recorded on an Onwood microammeter in parallel with a Tinsley universal shunt. All potentials e are against the saturated calomel electrode, e_0 for which is taken as 0·245 v on the hydrogen scale.

Results and Discussion

A graphite electrode in equilibrium with oxygen and alkaline peroxide solutions:

$$O_2 + H_2O + 2e \rightleftharpoons HO_2^- + OH^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

should set up a potential

$$e = e_0 + (\boldsymbol{R}T/2\boldsymbol{F}) \ln \{[p(O_2) \,.\, a(H_2O)/[a(OH^-) \,.\, a(HO_2^-)]\} \quad . \quad . \quad . \quad (i)$$

where $a(x)$ denotes the activity of species x. With $p(O_2) = 1$ atm. and $a(H_2O)$ taken as unity, a plot of e against log $[a(OH^-) \,.\, a(HO_2^-)]$ should be straight with slope −0·0296 v at 25° and intercept e_0. Our results (Table 1) confirm this. At these concentrations $a(HO_2^-)$ was taken as equal to the concentration of peroxide x as determined analytically, and $a(OH^-)$ to the activity of the original alkali minus x. Eqn. (i) can then be put as

$$e = e_0 - (\boldsymbol{R}T/2\boldsymbol{F})\{\ln [a(OH^-)_{\text{original}} - x] + \ln x\} \quad . \quad . \quad . \quad . \quad (1)$$

which on differentiation with respect to x gives

$$de/dx = (\boldsymbol{R}T/2\boldsymbol{F})\{1/[a(OH^-)_{\text{original}} - x] - 1/x\} \,. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From eqn. (2), a plot of e against x for one alkali concentration should give a curve having a minimum at $a(OH^-)_{\text{original}} = 2x$, as was substantiated from measurements in 0·1M-sodium hydroxide containing various concentrations of peroxide.

Although this interpretation differs from Berl's, our simple working electrode gives

Table 1. *Potential of the graphite electrode as a function of the peroxide ion activity at 25° in solutions saturated with 1 atm. of oxygen.*

$a(HO_2^-)$	$a(OH^-)$	* log $[a(OH^-) \,.\, a(HO_2^-)]$	e_h (mv)	$a(HO_2^-)$	$a(OH^-)$	* log $[a(OH^-)a(HO_2^-)]$	e_h (mv)
		0·1M-NaOH				1M-NaOH	
0·0007	0·0760	−4·2741	79	0·0006	0·699	−3·3773	50
0·0008	0·0758	−4·2172	73	0·0008	0·658	−3·2787	46
0·0013	0·0807	−3·9792	68	0·0010	0·671	−3·1733	43
0·0034	0·0755	−3·5906	57	0·0015	0·684	−2·9888	35
0·0050	0·0678	−3·4698	53	0·0028	0·662	−2·7319	31
0·0104	0·0626	−3·1864	44	0·0046	0·708	−2·4872	29
0·0259	0·0515	−2·8749	31	0·0101	0·655	−2·1795	15
0·0379	0·0410	−2·8086	29	0·0610	0·625	−1·4188	−10
0·0570	0·0204	−2·9345	34				

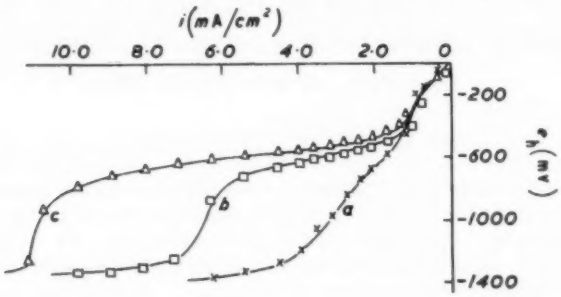
* Obtained from activity coefficients given by Harned and Owen (" The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, p. 560).

results in agreement with it. However, we obtain $e_0 = -49 \pm 3$ mv, as compared with Berl's value (on our sign convention) of −41·6 mv. For reaction (*a*) our value gives $\Delta G°(HO_2^-) = -16·8$ kcal. $mole^{-1}$, which is at least 1 kcal. higher than the usual values. [In this calculation we use the value $\Delta G°(OH^-) = -37·595$ kcal. $mole^{-1}$.[7]]

[7] Latimer, " Oxidation Potentials," Prentice-Hall, Inc., New York, 2nd edn., 1953, p. 39.

Although equilibrium was established almost instantaneously in oxygen-stirred solution of alkali containing peroxide, in the absence of peroxide the initial potential drifted and steady values of +40—+60 mv in 1·0M-sodium hydroxide were obtained only after 30—40 min. On cathodic polarisation at gradually increasing current densities, the potential of the electrode changed in a manner which depended greatly on the rate of stirring of the electrolyte (Fig. 2). With the stagnant electrolyte relatively small currents shift the potential to a resting stage which corresponds presumably to evolution of hydrogen. In the stirred electrolyte, however, two distinct depolarisation stages which

FIG. 3. *Current–potential curves obtained in* 1·0M-*sodium hydroxide vigorously stirred with oxygen with* (*a*) 0·0021, (*b*) 0·0092, *and* (*c*) 0·0180 *moles* $l.^{-1}$ *of hydrogen peroxide.*



indicate two different reduction processes occur before hydrogen begins to be evolved. In vigorously stirred electrolyte, the limiting current density, i_L, for the first reduction stage is about 0·8 mA /cm.^{2} of the geometrical surface area. From current-efficiency experiments (Table 2) this stage was shown to correspond to the reduction of oxygen almost quantitatively

TABLE 2.

Time (min.)	Current density (μA/cm.^{2})	$-e_h$ (mv) * Initial	Final	H_2O_2 yield (mg. $l.^{-1}$) Found †	Calc.	Efficiency (%)
90	588	115	118	69	70	98·5
90	588	117	116	67·2	70	96·0
180	588	116	120	137·6	140	92·8
180	588	112	117	130	140	92·8
90	1034	183	196	116	123	94·3
150	1034	186	200	189	205	92·7

* Electrode potential relative to the hydrogen electrode.
† Average from at least two analyses.

to hydrogen peroxide on the assumption of a two-electron transfer in the overall reaction. Results in Table 2 show that peroxide could also be formed at a pure graphite surface not previously activated with a current efficiency which, within the limits of accuracy of analysis, approximates to 100%; this result differs from that found by Berl.[2]

That the second depolarisation stage corresponds to the reduction of H_2O_2 (or HO_2^-) is shown by Fig. 3. The oxygen wave remains almost unaffected while the second wave becomes more stretched with the increase of peroxide concentration in such a manner that $i_L(\text{total}) - i_L(O_2)$ is almost proportional to $[H_2O_2]$. With pure hydrogen instead of oxygen the first wave disappeared completely and the potential fell directly to that of the second reduction stage. Under such conditions the above proportionality [with $i_L(O_2) = 0$] holds.

A pure graphite surface seems so far to be the only solid electrode on which the reduction

wave of both oxygen and hydrogen peroxide in alkaline solutions can be reproduced almost quantitatively as with a dropping-mercury cathode.[8] (With a rotating gold micro-electrode the hydrogen peroxide wave was ill-defined, and with an amalgamated silver electrode the waves were not reproducible.[9]) However, even on graphite the reduction mechanism is complex; thus for the oxygen-reduction step under limiting-current conditions, the equation

$$i_L = n\,FDC_0/\delta \qquad (b)$$

(where n is the number of electrons involved = 2, D is the diffusion coefficient of oxygen = $2{\cdot}6 \times 10^{-5}$ cm.^{2} sec.$^{-1}$,[10] C_0 the bulk concentration of oxygen in 1·0M-NaOH = $8{\cdot}3 \times 10^{-7}$ mole cm.$^{-3}$ [11]) gives for δ, the thickness of the diffusion layer, $5{\cdot}2 \times 10^{-3}$ cm., a value of the same order of magnitude as those obtained polarographically under similar conditions of stirring.[12] A plot of e_h against $\log[(i_L - i)/i]$ [13] yields, however, a straight line with slope 80—90 mv, which shows that the polarisation observed is not a purely concentration one, and that reduction does not proceed rapidly in one act according to $O_2 + H_2O + 2e \longrightarrow HO_2^- + OH^-$; the primary slow discharge of diffusing oxygen may be rate-determining. The state of the surface appears to be of primary importance in this respect. With short pieces of graphite previously heated under vacuum for about 2 hr. at 800—900°, then fitted as shown in Fig. 1, *B* to serve as electrodes, the course of oxygen reduction in oxygen-saturated 1·0M-sodium hydroxide differed fundamentally from that described above in that the potential during cathodic polarisation was independent of the rate of stirring of the electrolyte, although the general trend of the current–potential curve (broken curve in Fig. 2) was essentially the same as that obtained with the untreated electrode in the vigorously stirred electrolyte, and the yield of peroxide varied between 35 and 45% only of theory. At such a surface the reduction is probably of adsorbed oxygen to form adsorbed HO_2 radicals which may then undergo self-terminating chain reactions [14] leading to low peroxide yields. On untreated and heat-activated graphite surfaces the course of oxygen-reduction can be visualised as follows:

On untreated surface	On heat-activated surface
O_2(diffusing) + e $\longrightarrow$ O_2^- (slow)	$\gtrdot O_2$(adsorbed) + e $\longrightarrow$ $\gtrdot O_2^-$(adsorbed) (slow)
$O_2^- + H_2O + e \longrightarrow HO_2^- + OH^-$	$\gtrdot O_2^- + H_2O \longrightarrow \gtrdot O_2H + OH^-$
	$2\gtrdot O_2H + OH^- \longrightarrow HO_2^- + H_2O + O_2$
	or
	$2\gtrdot O_2H \longrightarrow H_2O + 1\frac{1}{2}O_2$

The half-wave potential of the peroxide wave lies (Fig. 3) at about −0·630 v, which is in close agreement with that reported by Bockris *et al.*[15] from measurements with the dropping-mercury cathode. For the three peroxide concentrations used the i_L values as calculated on the basis of equation (*b*) are roughly twice those obtained experimentally. We do not yet know whether the mechanism suggested by Bockris *et al.* to account for the splitting of the peroxide wave at mercury would still be applicable at graphite.

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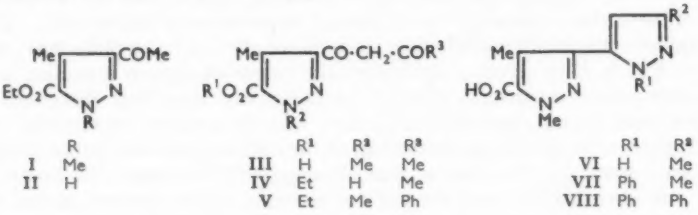
XUM

506. *Dipyrazolyls from C-Acetylpyrazoles.*

By E. G. Brain and I. L. Finar.

3-Acetylpyrazoles have been converted into pyrazolyl substituted β-diketones and benzylideneacetylpyrazoles. Both types of product have been used to prepare substituted dipyrazolyls: 3 : 5′-, 5 : 5′-, and 3 : 3′-dipyrazolyl have been obtained.

3 : 3′- and 3 : 5′-Dipyrazolyls have usually been prepared [1,2] from hydrazines and 1 : 3 : 4 : 6-tetraketones. The disadvantage of this method is that an unsymmetrical tetraketone can theoretically yield four dipyrazolyls, and a symmetrical tetraketone three. In one case [2] the intermediate pyrazolyl β-diketone was isolated and its structure elucidated. Since only two possible isomers can arise from a β-diketone and a hydrazine (cf. Finar and Simmonds [3]), the structures of the dipyrazolyls obtained from a pyrazolyl β-diketone can be ascertained more readily.



	R
I	Me
II	H

	R^1	R^2	R^3
III	H	Me	Me
IV	Et	H	Me
V	Et	Me	Ph

	R^1	R^2
VI	H	Me
VII	Ph	Me
VIII	Ph	Ph

Attempts to convert the ester group of ethyl 3-acetyl-1 : 4-dimethylpyrazole-5-carboxylate (I) into a β-dicarbonyl side-chain were unsuccessful but, when treated with ethyl acetate and sodium ethoxide, this ester gave 3-acetoacetyl-1 : 4-dimethylpyrazole-5-carboxylic acid (III). Under similar conditions the product from ethyl 5-acetyl-4-methylpyrazole-3-carboxylate (II) was the diketone ester (IV). When the ester (I) was condensed with ethyl benzoate the product was also a diketone ester (V).

With hydrazine, the acetoacetyl compound (III) gave 1 : 4 : 3′-trimethyl-3 : 5′-dipyrazolyl-5-carboxylic acid (VI). The product obtained by condensation with phenylhydrazine was assumed to have the structure (VII) by analogy with the formation of 3-methyl-1 : 5-diphenylpyrazole from benzoylacetone.[4]

Bromination of compound (VII) led to the 4′-bromo-derivative which, from molecular models, would be expected to be optically resolvable owing to restricted rotation about the C–C bond joining the pyrazole rings. An attempt to resolve this bromo-acid by means of the brucine salt was, however, unsuccessful. The alternative structure (XII) for the parent compound can, therefore, not be discounted.

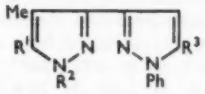
Ethyl 3-acetoacetyl-4-methylpyrazole-5-carboxylate (IV) also condensed with phenylhydrazine to give, after hydrolysis, a dipyrazolylcarboxylic acid (IX). This gave, on methylation, a mixture of the acid (VII) and its isomer (X). The orientation of the phenyl-substituted pyrazole ring in (IX) must therefore be as in (VII).

[1] Claisen and Roosen, *Annalen*, 1894, **278**, 294.
[2] Finar, *J.*, 1955, 1205.
[3] Finar and Simmonds, *J.*, 1958, 200.
[4] Drumm, *Proc. Roy. Irish Acad.*, 1931, **40**, *B*, 106.

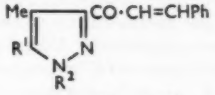
When ethyl 3-benzoylacetyl-1 : 4-dimethylpyrazole-5-carboxylate (V) was condensed with phenylhydrazine two products (VIII) and (XI) were obtained after hydrolysis. 1 : 4-Dimethyl-1′ : 5′-diphenyl-3 : 3′-dipyrazolyl-5-carboxylic acid (XI) was synthesised by an unambiguous method and was found to be identical with the minor product of the condensation. The major product is therefore 1 : 4-dimethyl-1′ : 3′-diphenyl-3 : 5′-dipyrazolyl-5-carboxylic acid (VIII). This is in contrast with the case of the pyrazolyl β-diketone previously quoted [2] which gave the 3 : 3′-dipyrazolyl as its major condensation product with phenylhydrazine.

The monobromo-derivative of the acid (VIII) could not be resolved by means of its brucine salt since the latter was obtained only as an uncrystallisable resin.

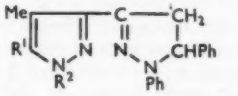
The unambiguous synthesis of 1 : 4-dimethyl-1′ : 5′-diphenyl-3 : 3′-dipyrazolyl-5-carboxylic acid (XI) was carried out in the following way. 3-Benzylideneacetyl-1 : 4-dimethylpyrazole-5-carboxylic acid (XV) was obtained by a Claisen–Schmidt reaction with the ethyl acetyldimethylpyrazolecarboxylate (I) and benzaldehyde. It did not react



	R^1	R^2	R^3
XI	CO_2H	Me	Ph
XII	CO_2H	Me	Me
XIII	CO_2H	H	Ph
XIV	H	Me	Ph



	R^1	R^3
XV	CO_2H	Me
XVI	H	Me
XVII	CO_2H	H



	R^1	R^3
XVIII	CO_2Me	Me
XIX	H	Me

satisfactorily with phenylhydrazine, the product being a mixture containing much unchanged starting material. Its methyl ester, however, afforded pure methyl 4′ : 5′-dihydro-1 : 4-dimethyl-1′ : 5′-diphenyl-3 : 3′-dipyrazolyl-5-carboxylate (XVIII). This was oxidised and then hydrolysed, to give the dipyrazolyl acid (XI).

In the same way, ethyl acetylmethylpyrazolecarboxylate (II) gave benzylideneacetylmethylpyrazolecarboxylic acid (XVII), which was condensed with phenylhydrazine and then oxidised to give 4-methyl-1′ : 5′-diphenyl-3 : 3′-dipyrazolyl-5-carboxylic acid (XIII).

The decarboxylation product (XVI) of the acid (XV) reacted with phenylhydrazine more completely than either the parent acid or its methyl ester, and the dihydrodipyrazolyl (XIX) was obtained. This gave 1 : 4-dimethyl-1′ : 5′-diphenyl-3 : 3′-dipyrazolyl (XIV) on oxidation.

Experimental

3-Acetoacetyl-1 : 4-dimethylpyrazole-5-carboxylic Acid.—Ethanol-free sodium ethoxide (2 mol., from 3·4 g. of sodium) was suspended in a refluxing mixture of ether (300 c.c.) and ethyl acetate (80 c.c.; excess) for 5 min., then ethyl 3-acetyl-1 : 4-dimethylpyrazole-5-carboxylate (15·6 g., 1 mol.) was added, and refluxing with stirring was maintained for 3 hr. A further 2 mol. of sodium ethoxide were then added, and refluxing and stirring were continued for another 3 hr. The mixture, which then contained a pale yellow precipitate, was extracted with water (200 c.c.) and then with N-sodium hydroxide (2 × 100 c.c.). The combined extracts were washed with ether and acidified with hydrochloric acid. From the sticky solid which was precipitated were obtained cream-coloured crystals of *3-acetoacetyl-1 : 4-dimethylpyrazole-5-carboxylic acid* by recrystallisation twice from benzene containing 5% of ethanol (yield 6·5 g., 39%; m. p. 179—180°) (Found: C, 53·1; H, 5·6; N, 12·7. $C_{10}H_{12}O_4N_2$ requires C, 53·6; H, 5·4; N, 12·5%).

If, instead of refluxing, the reactants were mixed and set aside at room temperature for 12 hr. the reaction failed. Low yields were obtained when the second addition of sodium ethoxide was omitted.

Ethyl 3-Benzoylacetyl-1 : 4-dimethylpyrazole-5-carboxylate.—The procedure given above was

repeated with ethyl benzoate instead of ethyl acetate. A yellow precipitate was formed during the refluxing but this was insoluble in water. It was therefore filtered off at the end of the reaction and then washed, first with ether, then with water. The pasty solid was shaken with ether (100 c.c.) and 4N-hydrochloric acid (30 c.c.). The ethereal layer was washed with water, dried (Na_2SO_4), and evaporated, leaving a solid. After three recrystallisations from ligroin pure *ethyl* 3-*benzoylacetyl*-1 : 4-*dimethylpyrazole*-5-*carboxylate* was obtained (5 g., 32%; m. p. 109°) (Found: C, 65·0; H, 5·9; N, 8·5. $C_{17}H_{18}O_4N_2$ requires C, 65·0; H, 5·7; N, 8·9%).

Ethyl 3-*Acetoacetyl*-4-*methylpyrazole*-5-*carboxylate*.—Claisen condensation with ethyl 5-acetyl-4-methylpyrazole-3-carboxylate and ethyl acetate was carried out as above but the proportion of ethyl acetate to ether used as solvent was kept high (approx. 50% by vol.) since larger amounts of ether resulted in the precipitation of the *N*-sodium salt of the acetylpyrazole. The product was worked up as for 3-acetoacetyl-1 : 4-dimethylpyrazole-5-carboxylic acid but, after recrystallisation from benzene, the product was found to be the *ester* (28%; m. p. 121—123°). A further recrystallisation from benzene raised the m. p. to 123—124° (Found: C, 55·8; H, 6·0; N, 12·0. $C_{11}H_{14}O_4N_2$ requires C, 55·5; H, 5·9; N, 11·8%).

Condensation of 3-*Acetoacetyl*-1 : 4-*dimethylpyrazole*-5-*carboxylic Acid with Hydrazine*.—A mixture of the diketone (2·0 g., 1 mol.), 60% hydrazine hydrate (0·82 g., 1·1 mol.), and ethanol (30 c.c.) was heated for 30 min. on the steam-bath. Water was added and the solution was cooled. A brown mass of crystals was deposited. When twice recrystallised from water this yielded pure 1 : 4 : 3′-*trimethyl*-3 : 5′-*dipyrazolyl*-5-*carboxylic acid*, m. p. 247—248° (decomp.) (Found: C, 54·3; H, 5·5; N, 25·7. $C_{10}H_{12}O_2N_4$ requires C, 54·5; H, 5·45; N, 25·45%).

Condensation of 3-*Acetoacetyl*-1 : 4-*dimethylpyrazole*-5-*carboxylic Acid with Phenylhydrazine*.—The diketone (2 g., 1 mol.), phenylhydrazine (1·9 g., 2 mol.) and acetic acid (25 c.c.) were refluxed together for 2·5 hr. Water (20 c.c.) was added. 1 : 4 : 3′-*Trimethyl*-1′-*phenyl*-3 : 5′-*dipyrazolyl*-5-*carboxylic acid* slowly separated. This was recrystallised, first from benzene–ligroin, then twice from dilute ethanol and had m. p. 212—213° (1·1 g.) (Found: C, 64·5; H, 5·4; N, 18·7. $C_{16}H_{16}O_2N_4$ requires C, 64·8; H, 5·4; N, 18·9%).

The acid was brominated in chloroform solution and the resulting 4′-*bromo*-1 : 4 : 3′-*trimethyl*-1′-*phenyl*-3 : 5′-*dipyrazolyl*-5-*carboxylic acid* was obtained as white crystals, m. p. 201·5—202·5°, from hot dilute ethanol (Found: C, 51·7; H, 4·0; N, 15·0; Br, 21·5. $C_{16}H_{15}O_2N_4Br$ requires C, 51·2; H, 4·0; N, 14·95; Br, 21·35%). A hydrated product, m. p. 110° (decomp.), is obtained from cold dilute ethanol.

Condensation of Ethyl 3-*Acetoacetyl*-4-*methylpyrazole*-5-*carboxylate with Phenylhydrazine*.—This was carried out as described for the *N*-methyl derivative, but the product, an oil, was saponified with ethanolic potassium hydroxide, to yield, on acidification with dilute hydrochloric acid, 4 : 3′-*dimethyl*-1′-*phenyl*-3 : 5′-*dipyrazolyl*-5-*carboxylic acid* which, recrystallised from dilute ethanol and then ethanol, had m. p. 250—251° (Found: C, 63·7; H, 4·8; N, 19·8. $C_{15}H_{14}O_2N_4$ requires C, 63·8; H, 4·95; N, 19·85%). No other product was isolated.

This acid (2·3 g.) was treated with methyl sulphate (1 mol.) and sodium hydroxide (2·5 mol.) in aqueous solution at 90°. After 1 hr. the solution was acidified. The precipitated oil solidified and was dried, giving a buff powder (2·15 g.), m. p. *ca.* 60—90°. This was recrystallised twice from benzene (100 c.c.), to give white needles of 1 : 4 : 3′-trimethyl-1′-phenyl-5 : 5′-dipyrazolyl-3-carboxyiic acid, m. p. 232·5—233° (Found: C, 64·5; H, 5·1; N, 18·8. $C_{16}H_{14}O_2N_4$ requires C, 64·8; H, 5·4; N, 18·9%). Concentration of the original benzene mother-liquor gave a second crop consisting of a mixture of the above compound together with blunt crystals of the already known 1 : 4 : 3′-trimethyl-1′-phenyl-3 : 5′-dipyrazolyl-5-carboxylic acid. The fine needles were mechanically removed from the blunt crystals by a stream of light petroleum. The blunt crystals were then recrystallised from benzene–ligroin and from dilute ethanol, having m. p. 210·5—212°, mixed m. p. 212—213° with an authentic specimen.

Condensation of Ethyl 3-*Benzoylacetyl*-1 : 4-*dimethylpyrazole*-5-*carboxylate with Phenylhydrazine*.—This was carried out by the usual method. In this case also the product was an oil and was therefore saponified to give the solid dipyrazolyl acid. The yield of crude acid (m. p. 185—190°) was 91·5%. This was recrystallised four times from benzene containing 10% of ligroin: pure 1 : 4-*dimethyl*-1′ : 3′-*diphenyl*-3 : 5′-*dipyrazolyl*-5-*carboxylic acid* (52%) had m. p. 193—194° (Found: C, 70·2; H, 5·2; N, 15·6. $C_{21}H_{18}O_2N_4$ requires C, 70·3; H, 5·0; N, 15·65%).

The recrystallisation liquors were worked up by the usual procedure for fractional crystallisation and a more soluble fraction (m. p. 184—212°; 8·4%) was thus obtained. After two

recrystallisations from ethanol 1 : 4-dimethyl-1′ : 5′-diphenyl-3 : 3′-dipyrazolyl-5-carboxylic acid (0·3%), m. p. and mixed m. p. 256—256·5°, was obtained.

3-Benzylideneacetyl-1 : 4-dimethylpyrazole-5-carboxylic Acid.—A mixture of ethyl 3-acetyl-1 : 4-dimethylpyrazole-5-carboxylate (2·0 g., 0·95 mol.), benzaldehyde (1·06 g., 1 mol.), 10% aqueous sodium hydroxide (20 c.c.; excess), and ethanol (50 c.c.) was set aside for 20 hr., then acidified. The white precipitate of the *benzylideneacetyldimethylpyrazolecarboxylic acid* (1·7 g.), recrystallised from ethanol, had m. p. 267—268° (decomp.) (1·3 g., 46%) (Found: C, 66·4; H, 5·2; N, 10·5. $C_{15}H_{14}O_3N_2$ requires C, 66·7; H, 5·2; N, 10·4%).

This acid was refluxed for 30 hr. with methanol (40 c.c.) and saturated methanolic hydrogen chloride (20 c.c.). The mixture was then cooled and the solid filtered off. Three recrystallisations from ethanol gave the *methyl ester*, m. p. 177—178° (Found: C, 67·7; H, 5·85; N, 9·6. $C_{16}H_{16}O_3N_2$ requires C, 67·5; H, 5·65; N, 9·85%).

The acid was heated at 280° for 25 min. The tarry product was washed in ether with aqueous sodium hydroxide and passed through alumina. The crude *3-benzylideneacetyl-1 : 4-dimethylpyrazole* then obtained by evaporation was recrystallised from ligroin (63%; m. p. 90—92°). Two more recrystallisations raised the m. p. to 92·5—93·5° (Found: C, 74·1; H, 6·1; N, 12·8. $C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2; N, 12·4%).

Benzylideneacetyldimethylpyrazole was condensed with phenylhydrazine by the method used for the diketone. *1 : 2-Dihydro-1′ : 4′-dimethyl-1 : 5-diphenyl-3 : 3′-dipyrazolyl* was obtained; it formed colourless crystals, m. p. 141—142° (50%), from ligroin (Found: C, 75·8; H, 6·3; N, 17·3. $C_{20}H_{20}N_4$ requires C, 75·9; H, 6·3; N, 17·7%). Solutions of this substance in ligroin gave a strong blue fluorescence in ultraviolet light. Oxidation with potassium permanganate in acetone then gave *1 : 4-dimethyl-1′ : 5′-diphenyl-3 : 3′-dipyrazolyl* which, when twice recrystallised from ligroin, melted at 139—141° (mixed m. p. with the precursor 117—127°) (Found: C, 76·6; H, 5·8; N, 18·0. $C_{20}H_{18}N_4$ requires C, 76·4; H, 5·7; N, 17·8%).

Methyl 4′ : 5′-Dihydro-1 : 4-dimethyl-1′ : 5′-diphenyl-3 : 3′-dipyrazolyl-5-carboxylate.—Methyl 3-benzylideneacetyl-1 : 4-dimethylpyrazole-5-carboxylate was condensed with phenylhydrazine by the usual method but with refluxing for 8 hr. The *product* was obtained by recrystallisation from ethanol as blunt crystals, m. p. 174—175°, strongly fluorescent in ultraviolet light (Found: C, 70·6; H, 5·8; N, 15·0. $C_{22}H_{22}O_2N_4$ requires C, 70·6; H, 5·9; N, 15·0%).

Oxidation with potassium permanganate in 90% aqueous pyridine gave the fully aromatic dipyrazolyl ester, m. p. 128—129°, which was hydrolysed by ethanolic potassium hydroxide to 1 : 4-dimethyl-1′ : 5′-diphenyl-3 : 3′-dipyrazolyl-5-carboxylic acid, m. p. 255—256° (decomp.) (from ethanol) (Found: C, 69·9; H, 4·9; N, 15·2. $C_{21}H_{16}O_2N_4$ requires C, 70·3; H, 5·0; N, 15·65%).

5-Benzylideneacetyl-4-methylpyrazole-3-carboxylic Acid.—Ethyl 5-acetyl-4-methylpyrazole-3-carboxylate was condensed with benzaldehyde by the method previously used, but the reaction was allowed to proceed for 1·5 days. The *benzylideneacetylmethylpyrazole acid*, crystallised from acetic acid, had m. p. 231·5—233° (Found: C, 66·0; H, 4·3; N, 11·1. $C_{14}H_{12}O_3N_2$ requires C, 65·6; H, 4·7; N, 10·95%).

4′-Methyl-1 : 5-diphenyl-3 : 3′-dipyrazolyl-5′-carboxylic Acid.—The above benzylidene compound was condensed with phenylhydrazine by the general method and refluxed for 7 hr. The crude product was not purified but oxidised directly by permanganate–pyridine. The final pyridine solution was evaporated and the residue dissolved in a little water and then acidified. The precipitated *acid* had m. p. 273·5—274° (decomp.) (from acetic acid) (Found: C, 69·25; H, 5·4; N, 16·1. $C_{20}H_{20}O_2N_4$ requires C, 69·0; H, 5·75; N, 16·1%).

One of us (E. G. B.) thanks the D.S.I.R. for a maintenance grant.

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XUM

507. *The Heat of Solution of Plutonium Trichloride.*

By (Miss) P. E. Martin and A. G. White.

The heat of solution of anhydrous plutonium trichloride in aqueous perchloric acid and in perchloric acid–lithium perchlorate solutions at constant ionic strength has been measured. The results provide further evidence for the formation of a chloride complex by the tervalent plutonium ion and an approximate value for the change of heat content accompanying its formation has been calculated.

Some measurements of the heat of solution of plutonium trichloride in hydrochloric acid have been reported by Westrum and Robinson.[1] The heat of solution varied markedly with the acid concentration, as is the case with uranium [2] and thorium tetrachloride,[3] but the data do not suffice to indicate whether this variation is due to increasing complex-ion formation, changing ionic strength, or a specific variation of the true heat of solvation of the ions with hydrogen-ion concentration. Therefore measurements are now reported of the heat of solution in perchloric acid and in perchloric acid–lithium perchlorate solutions. A comparison of the former with the previous results [1] should show the effect of complex-ion formation, while the latter will demonstrate the effects of ionic strength and hydrogen-ion concentration.

Experimental

Glove-box techniques were used throughout the work.

Anhydrous plutonium trichloride was supplied by Mr. J. H. Freeman of General Physics Division, A.E.R.E., to whom we are much indebted. It contained a small amount of insoluble matter and analysis indicated 96·5% of $PuCl_3$. Chloride was determined volumetrically with silver nitrate, and plutonium by alpha-particle counting with a low-geometry counter, the two methods giving excellent agreement.

As plutonium trichloride is very hygroscopic it was handled under dry conditions and the calorimetric samples (approx. 40 mg.) were weighed out and sealed into the thin glass sample-bulbs (5 mm. in diameter) as described for uranium tetrachloride.[2]

The general arrangement of the calorimeter closely resembled that described by Westrum and Eyring.[4] The calorimeter vessel was of stainless steel, 2 inches in diameter and 2¾ inches deep. It was suspended from a Perspex support (cf. ref. 4) inside a brass "submarine" and the dead-air gap was 1·2 cm. The normal charge was 70 ml. of solution. In place of the quartz shaft used by Westrum and Eyring a thin-walled stainless-steel tube carrying a stainless-steel rod at the end passed axially through a polytetrafluoroethylene bush in the calorimeter lid and carried the sample-bulb which was waxed to the end of the rod. This tube was spring-loaded and the sample-bulb could be broken against a projection on the floor of the vessel by removing a pin which released the spring. Stirring was carried out by oscillating the entire assembly through approx. 120° at a rate of 117 strokes per min. Tests with permanganate and a glass vessel showed this to be satisfactory.

Temperature measurements were made with two 1000 ohm nickel resistance thermometers, in opposite arms of a bridge network, which were wound on the outside of the calorimeter vessel. This vessel also carried a further winding, of 50 ohms of manganin, for the calibration heater. The output from the thermometer bridge was taken to a D.C. amplifier and from thence to a Brown potentiometer-recorder to give a continuous time–temperature record. The heat-input and timing arrangements for the calibration heater were as described previously.[5]

The entire calorimeter was immersed in water in a large Dewar vessel (15 cm. in diameter and 28·5 cm. deep) suspended in a water-bath (±0·001°). The working temperature was 25·0°.

[1] Westrum and Robinson, Paper 6.54, "The Transuranium Elements," Vol. 14B, National Nuclear Energy Series, McGraw Hill, New York, 1949.
[2] Hearne and White, *J.*, 1957, 2081.
[3] Westrum and Robinson, ref. 1, Paper 6.50.
[4] Westrum and Eyring, *J. Amer. Chem. Soc.*, 1952, **74**, 2045.
[5] Salman and White, *J.*, 1957, 3197.

Results and Discussion

The heats of solution of plutonium trichloride in perchloric acid–lithium perchlorate solutions at a constant ionic strength (μ) 2·0 and in perchloric acid at various values of μ were measured and are presented in Table 1. For comparison Table 2 contains the results obtained by Westrum and Robinson [1] for the heat of solution in hydrochloric acid. At

Table 1. *Heat of solution of plutonium trichloride in aqueous perchlorate solutions at 25·0°.*

Final plutonium concn. $1·5 \times 10^{-3}$M.

$[HClO_4]$ (M)	$[LiClO_4]$ (M)	μ	Heat evolved (kcal./mole of $PuCl_3$)
0·1	1·9	2·0	31·67; 31·25
0·5	1·5	2·0	30·23; 30·31
1·0	1·0	2·0	30·58; 30·18
1·5	0·5	2·0	30·44; 30·56; 30·73
2·0	0	2·0	28·29; 28·55
1·5	0	1·5	31·49; 31·02
0·1	0	0·1	33·15; 32·90

Table 2. *Heat of solution of plutonium trichloride in hydrochloric acid at 25°.*

[HCl]	0·1	1·5	6·0	9·0	11·38
Heat evolved (kcal./mole of $PuCl_3$)	31·76	29·43; 29·57	22·14; 22·20; 22·15	14·54	(9·8—10·2)

acid concentrations of 0·1M and 1·5M the heat of solution is markedly lower in hydrochloric than in perchloric acid. This confirms the belief that tervalent plutonium is appreciably involved in complex-formation in chloride solutions (this conclusion would not be valid if replacement of chloride ion by perchlorate affected the solvation energies of the ions). Ward and Welch [6] used an ion-exchange method to determine equilibrium constants for reaction (*A*) at 21° ± 1°, and at ionic strengths of 0·2, 0·5, and 1·0 the values of

$$PuCl^{2+} \rightleftharpoons Pu^{3+} + Cl^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

the equilibrium constant, K, obtained were 0·44, 0·57, and 1·1 g.-ion $l.^{-1}$ respectively. Extrapolation of Ward and Welch's data to ionic strengths of 0·1 and 1·5 would enable the heat content change, ΔH, associated with reaction (*A*) to be calculated from the values given in Tables 1 and 2 as follows.

Let the equilibrium constant of (*A*) be K:

$$K = [Pu^{3+}][Cl^-]/[PuCl^{2+}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and assume that the concentration of free chloride ion in the hydrochloric acid solutions is the analytical HCl concentration and that the extent of chloride-complex formation in the perchloric acid solutions is negligible (in view of the very low Pu^{3+} concentrations these assumptions should be valid). The difference between the heat of solution in HCl, ΔH_s^1, and the heat of solution in perchloric acid at the same concentration, ΔH_s^2, will be due to the heat effect produced by the dissociation of that fraction of the total plutonium which is present as $PuCl^{2+}$ in the hydrochloric acid solution, so that:

$$\Delta H_s^2 - \Delta H_s^1 = (1 - [Pu^{3+}]/[Pu]_T)\Delta H \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

$$[Pu]_T = [Pu^{3+}] + [PuCl^{2+}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From (1) and (3), $(1 - [Pu^{3+}]/[Pu]_T) = [Cl^-]/(K + [Cl^-])$

Hence

$$\Delta H = (\Delta H_s^2 - \Delta H_s^1)(K + [Cl^-])/[Cl^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Ward and Welch used Davies's empirical equation [7] to extrapolate their values of K to zero ionic strength. They state, however, that their value of K at $\mu = 1·0$ is of doubtful validity as there is an indication in their experimental results that at the chloride-ion

[6] Ward and Welch, *J. Inorg. Nucl. Chem.*, 1956, **2**, 395; personal communication.
[7] Davies, *J.*, 1938, 2093.

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concentration used, 1·0M, dichloro-complex formation also occurred to a considerable extent. Thus it would be pointless to attempt an extrapolation to $\mu = 1{\cdot}5$ where in hydrochloric acid even more dichloro-complex formation would be expected. We have, therefore, carried out the extrapolation (by means of the Davies equation) only for $\mu = 0{\cdot}1$ at which value we find $K = 0{\cdot}299$ at Ward and Welch's temperature of 21°. As this temperature is rather far from our experimental temperature of 25° we have calculated ΔH by successive approximations, the value of $K = 0{\cdot}299$ first being used in equation (4) to give an approximate value of ΔH which was then used to correct K to 25°, the corrected value of K then being used to give a more accurate value of ΔH, and the whole process repeated until the value of ΔH obtained no longer varied.

By this means we have obtained values of $\Delta H = -4{\cdot}6$ kcal./mole and $K = 0{\cdot}269$ at 25° and $\mu = 0{\cdot}1$. From these values the free-energy and entropy changes associated with reaction (*A*) at $\mu = 0{\cdot}1$ can be calculated and are $\Delta F = +0{\cdot}78$ kcal./mole and $\Delta S = -18$ entropy units. The entropy change may be correlated with the changes in charge of the reactants which will produce a fairly large change in the extent of solvation, the dissociation of the $PuCl^{2+}$ ion to give the Pu^{3+} ion being accompanied by an increase in the ordering of the solvent and hence a marked decrease in entropy.

The series of results at $\mu = 2{\cdot}0$, given in Table 1, show that in contrast to results with uranium tetrachloride [2] there is no marked specific effect of the hydrogen ion on the heat of solvation until the concentration of this species exceeds 1·5M (we are unable to explain the rise at 0·1M). With uranium tetrachloride there is a rapid decrease in the heat of solution, at constant ionic strength, from hydrogen-ion concentrations of 0·5M onwards. If, as suggested by Samoilov,[8] the effect is largely electrostatic in origin and due to the statistical spreading of the hydrogen-ion charge over all available water molecules, then this difference in behaviour is qualitatively understandable. The lower charge on the Pu^{3+} ion than on the U^{4+} ion would require a higher concentration of hydrogen ion to produce a given repulsive effect.

We thank Mr. T. L. Markin for performing the plutonium analyses.

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[*Present Address* (A. G. W): TECHNICAL COLLEGE, COVENTRY.] [*Received, February 12th,* 1958.]

[8] Samoilov, *Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, 641.

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508. *The Crystal Structures of Some Analogues of Perylene.*

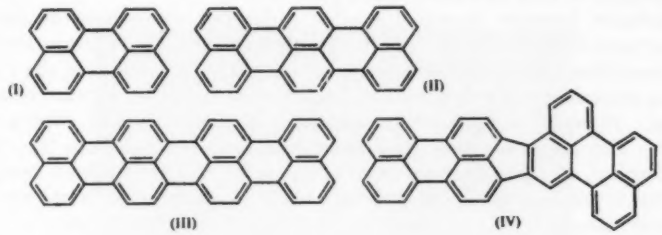
By E. CLAR and J. C. SPEAKMAN.

By comparing some of the crystallographic properties of terrylene (II) and quaterrylene (III) with those of perylene (I), the assignment of formulæ to the first two hydrocarbons is confirmed. Corresponding *X*-ray diffraction photographs of all three compounds are strikingly similar, proving that the arrangement of the respective molecules in their crystals is almost identical.

THE crystal structure of perylene (I) was determined by Donaldson, Robertson, and White.[1] The second member in the series of *peri*-condensed naphthalene analogues (II), terrylene, has been synthesised by Clar, Kelly, and Laird,[2] who described it as a deep red hydrocarbon, m. p. 510°. The third member (III), quaterrylene, was described [2] as a very dark green compound, m. p. >570°. It had been obtained from a sodium chloride–aluminium chloride melt of perylene. However, the products also included a red-brown hydrocarbon, m. p. 467—469°, which must have originated in some other mode of combination of two perylene molecules, *e.g.* (IV). There might therefore be some error in the identification of the green hydrocarbon with quaterrylene. For instance, Zinke, Nussmüller, and

[1] Donaldson, Robertson, and White, *Proc. Roy. Soc.*, 1953, *A*, **220**, 311.
[2] Clar, Kelly, and Laird, *Monatsh.*, 1956, **87**, 391.

Ott [3] believed they had synthesised quaterrylene from perylene and 1-bromonaphthalene, whereas their product has been shown to be terrylene.[3] Since series of similarly analogous aromatic hydrocarbons often have closely related crystal structures,[4] a comparison of the



crystallographic properties of these two hydrocarbons with those of perylene might provide conclusive evidence that the compounds are indeed related as formulæ (I)—(III) require.

Experimental

Crystals of the red hydrocarbon, obtained from trichlorobenzene, consisted of small rectangular leaflets, with the (001) face as the only form to show appreciable development. Viewed normally to this face in polarised light, the crystals gave oblique extinction and marked pleochroism. Though they were too thin for easy handling, several *X*-ray rotation and oscillation photographs were obtained at various settings of a single crystal. From them it was possible to derive approximate values for the unit-cell parameters (see Table).

Unit-cell parameters.

		a	*b*	*c*	*β*	d_m	d_c	*Z*	Space group
Perylene	$C_{20}H_{12}$	11·35	10·87	10·31	101°	1·32	1·342	4	$P2_1/a$
Terrylene	$C_{30}H_{16}$	11·$_4$	10·7	14·$_2$	(102°)	—	1·42	4	$P2_1/a$
Quaterrylene ...	$C_{40}H_{20}$	11·4	10·6$_2$	19·7	103°	1·42	1·429	4	$P2_1/a$

More satisfactory crystals of the green hydrocarbon were grown by sublimation. Again rectangular and with the (001) face most prominently developed, they possessed a number of other faces. Lying on the (001) face, the platelets normally appeared black, though—when thin enough—they were dark green, with oblique extinction. Viewed in an edge-on aspect, they showed a less intense colour, despite the fact that the transmitted light then had to traverse a greater thickness of material. The unit-cell parameters listed in the Table were derived from an adequate set of rotation, oscillation, and moving-film photographs. Copper K_α-radiation was used. The data shown for perylene are those cited by Robertson.[4] Axial translations are in Å, d_m is the measured density found by flotation and d_c that calculated, and Z is the number of molecules per unit cell. Different crystals of quaterrylene appeared to differ appreciably in density; the value given has been biased in favour of the higher densities observed. The space group of terrylene was not completely determined, but no reflexions inconsistent with $P2_1/a$ were recorded, and this group appears to be fully justified by the considerations set out below.

Discussion

These parameters correspond closely: *a* and *b* are nearly the same for all three compounds, whilst there are successive increments of about 4·7 Å in *c*. The length of molecules (I)—(III) would be expected to increase successively by about 4·3 Å, made up of 2·8 Å, the distance between atoms 1 and 4 in a naphthalene residue, and of 1·5 Å, the length of the *peri*-bond. The small discrepancy between 4·7 and 4·3 Å may be attributed to the

[3] Zinke, Nussmüller, and Ott, *Monotsh.*, 1955, **86**, 853.
[4] Robertson, "Organic Crystals and Molecules," Cornell Univ. Press, 1953, p. 216.

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longer molecules' being packed more nearly parallel to the *c*-axis, as is also suggested by the significantly lower value of *b* for quaterrylene. On the evidence of these unit-cell dimensions alone, it is likely that the three compounds are perylene and its analogues, with the greatest lengths of their molecules nearly parallel to *c*.

This conclusion becomes inescapable after a detailed comparison of corresponding *X*-ray photographs has been made. With due allowance for the different lengths of the *c*-axes, the resemblance was very close in every case. It is illustrated in the Plate, where [110] rotation photographs of perylene and quaterrylene are shown separately and then in juxtaposition. In some respects the resemblance is closer without allowance for the changes in *c*. This arises because the Fourier transforms of molecules (I)—(III) are in large part identical, so that—the molecules of the different hydrocarbons being similarly arranged in the crystals—intense reflexions are likely to occur in the same region of corresponding *X*-ray diagrams, irrespective of the particular value of the *l*-index.

There can be no doubt that these crystals are built from closely analogous molecules, arranged in an almost identical manner. It follows that, since the crystal structure of perylene is already known, those of terrylene and quaterrylene can be immediately inferred to a good first approximation. A more detailed study of quaterrylene will be undertaken, though the structure—like that of perylene—is not one that lends itself to accurate analysis by two-dimensional methods.

These three compounds constitute a crystallographic series whose regularity is almost equal to that shown by the normal paraffins and their derivatives. Diphenyl, terphenyl, and quaterphenyl are a comparable family;[5] with each additional phenyl group the *c*-axis increases by about 4·2 Å, as would be expected. (The crystallographic evidence—which is self-consistent, though of an early date[6]—requires each of these molecules to be centrosymmetric, and probably coplanar; but, in the gaseous state, that of diphenyl is not so.[7]) A similar and longer series occurs with naphthalene and its benzologues, which have been studied as far as hexacene;[4] but, though the unit cells correspond, there is a change from monoclinic to triclinic symmetry between anthracene and tetracene. Respective *c*-axes increase by about 2·4 Å, which agrees with the expected increase in molecular length. In the series, coronene–ovalene–circumanthrene,[8] the increment appears in the *a*-axis, and averages at about 3·5 Å, which is greater than the increase in molecular length, 2·4 Å. This increase lies approximately in the direction of the *a*-glide, so that two molecules, rather steeply inclined to *a*, come within the primitive translation.

Thanks are expressed to Professor J. M. Robertson, F.R.S., for his interest and encouragement, and to Imperial Chemical Industries Limited for supplying some of the equipment.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW, W.2. [*Received, January 29th,* 1958.]

[5] Pickett, *Nature*, 1933, **131**, 513.
[6] *Idem*, *J. Amer. Chem. Soc.*, 1936, **58**, 2299; earlier references are also given here, or in *Strukturbericht*.
[7] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408.
[8] Clar, Kelly, Robertson, and Rossmann, *J.*, 1956, 3878.

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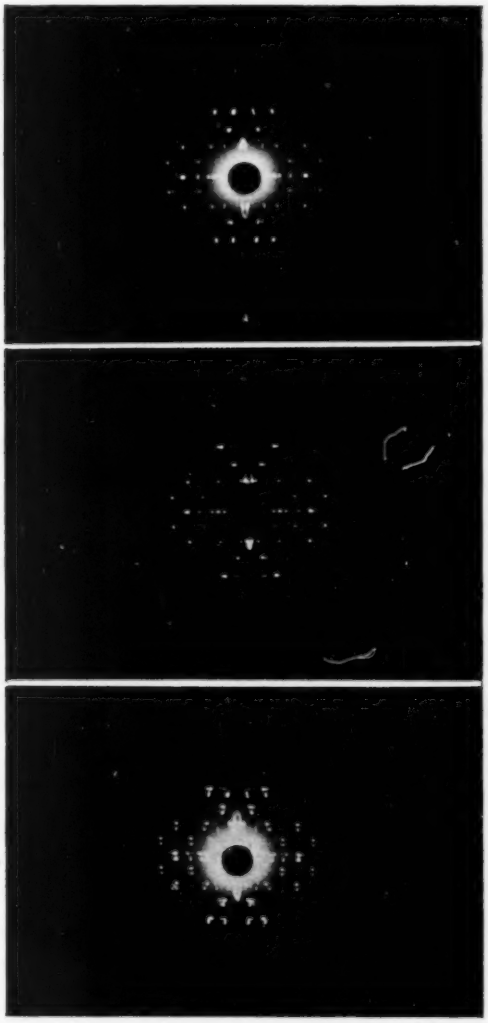
A comparison of [110] *rotation* X*-ray diagrams for crystals of perylene and quaterrylene.* (a) *Perylene.* (b) *Quaterrylene.* (c) *Both diagrams* (a) *and* (b) *in closer juxtaposition.* (*That for quaterrylene has been displaced upwards by about* 1 *mm.*).



(a)

(b)

(c)

[*To face p.* 2494.

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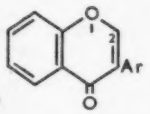
509. *The Synthesis of* iso*Flavones.*

By J. E. Gowan, M. F. Lynch, N. S. O'Connor, (Mrs.) E. M. Philbin, and T. S. Wheeler.

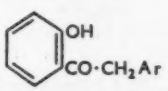
*iso*Flavones are obtained, in some instances in satisfactory yield, by the action of formanilide or formamide on benzyl *o*-hydroxyphenyl ketones. 2-Substituted *iso*flavones can be prepared by heating *o*-acyloxyphenyl benzyl ketones.

Various sources of the $C_{(2)}$-atom in *iso*flavones (I) which would permit of their ready synthesis from benzyl *o*-hydroxyphenyl ketones (2-hydroxydeoxybenzoins) (II) have been investigated.[1] It has now been found that formamide, or preferably formanilide, can in some instances supply the necessary $C_{(2)}$-atom, with yields of *iso*flavone of up to 60%. The technique is simple: the amide and the deoxybenzoin are heated together for about 30 min.; normally the isolation of the *iso*flavone presents little difficulty. The results are summarised in Table 3 and a list of unreactive deoxybenzoins is given on p. 2498.

It is necessary to protect hydroxyl groups in the deoxybenzoin, except that in the 2-position. Electron-attracting radicals, *e.g.*, benzoyl, *p*-nitrobenzoyl, toluene-*p*-sulphonyl, give much better results than the methyl group which tends to inhibit the reaction. Dearoylation occurs when the benzoyl or *p*-nitrobenzoyl derivatives are employed; the products obtained with the latter are harder to purify. The toluene-*p*-sulphonyl group promotes good yields but is difficult to remove from the resulting *iso*flavone, being resistant to the action of cold sulphuric acid, hydrochloric acid in acetic acid at 100°, and refluxing dilute ethanolic potassium hydroxide, though it is smoothly eliminated by hydriodic acid in acetic anhydride under demethylating conditions.



(I)



(II)

The use of esterification for protection of hydroxyl groups is limited. It was not possible to prepare the 4 : 6-di-*O*-benzoyl or -di-*O*-toluene-*p*-sulphonyl derivative of benzyl 2 : 4 : 6-trihydroxyphenyl ketone.

The introduction of a nitro-group in the 4'-position in the deoxybenzoin is advantageous.[2,3] Benzyl 2-hydroxy-4 : 6-dimethoxyphenyl ketone gives no *iso*flavone, while with the corresponding 4-nitrobenzyl ketone yields of 15% (formamide) and 25% (formanilide) are obtained. The production of *iso*flavone is not increased by the use of sulphuric acid as condensing agent, or by addition of formic acid as in the Leukart–Wallach reaction.

The reaction, while useful in particular cases, does not displace as the method of choice the ethoxalyl chloride process [4] which can be employed with polyhydroxydeoxybenzoins without protection of the hydroxyl groups. This advantage also attaches to the method recently described by Farkas [5] in which the $C_{(2)}$-atom is obtained by the action of hydrogen chloride on zinc cyanide.

No useful result was achieved in efforts to extend the scope of the new reaction. A series of experiments in which various 2-hydroxy- and 2-hydroxy-ω-methoxy-acetophenones

[1] Baker and Ollis, *Sci. Proc. Roy. Dublin Soc.*, 1956, **27**, 119; Warburton, *Quart. Rev.*, 1954, **8**, 67.
[2] Iyer, Shah, and Venkataraman, *Proc. Indian Acad. Sci.*, 1951, **33**, *A*, 116.
[3] Dutta and Bose, *J. Sci. Ind. Res., India*, 1952, **11**, *B*, 413.
[4] (*a*) Baker, Chadderton, Harborne, and Ollis, *J.*, 1953, 1852; (*b*) Baker, Harborne, and Ollis, *ibid.*, p. 1860.
[5] Farkas, *Chem. and Ind.*, 1957, 1212; *Chem. Ber.*, 1957, **90**, 2940.

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were heated with formamide or formanilide with view to production of chromones did not give identifiable products.

The possibility of a thermally induced Baker–Venkataraman transformation of *o*-acyloxyacetoarones into the corresponding *o*-hydroxy-1 : 3-diketone or flavone was first shown by Venkataraman [6] and later studied in this laboratory (see, for example, O'Toole and Wheeler [7]). Heating alone or in glycerol was employed. It has now been found (see Table 4) that 2-acyloxydeoxybenzoins when heated at 250° give the corresponding 2-substituted *iso*flavones, in some instances in satisfactory yield. This reaction parallels the ready manner in which these compounds undergo the Baker–Venkataraman base-catalysed transformation,[8] which may also be brought about thermally.[6,7] As in the formamide method polyhydroxydeoxybenzoins do not react well. No advantage was obtained by using glycerol as a solvent.

Experimental

The methods used in the preparation mentioned in Tables 1 and 2 were: (1) acetylation by acetic anhydride and a trace of perchloric acid; (2) methylation by methyl sulphate, acetone, and potassium carbonate; (3) esterification by pyridine and acid chloride; (4) sulphonylation by toluene-*p*-sulphonyl chloride, acetone, and potassium carbonate; (5) Schotten–Baumann method.

Table 1. *Deoxybenzoins (benzyl phenyl ketones) prepared by methods other than those given for them in the literature.*

Deoxybenzoin	Ketone from which prepared	Method (see text)	Form (solvent)	M. p. (found)	M. p. (lit.)
Benzyl 2 : 4-diacetoxyphenyl ketone	Benzyl 2 : 4-dihydroxyphenyl [a]	1	Needles (AcOH)	135—136°	136° [b]
Benzyl 2 : 4-dibenzoyloxyphenyl ketone	" "	3	Yellow needles (AcOH)	110—112	95—96° [c]
2-Hydroxy-4-methoxyphenyl 4-nitrobenzyl ketone	2 : 4-Dihydroxyphenyl 4-nitrobenzyl [d]	2	Plates (EtOH)	134—136	136° [d]
2-Hydroxy-4 : 6-dimethoxyphenyl 4-nitrobenzyl ketone	4-Nitrobenzyl 2 : 4 : 6-trihydroxyphenyl [e]	2	Needles (EtOH)	150	148
Benzyl 2-hydroxy-4 : 5-dimethoxyphenyl ketone	Benzyl 2 : 5-dihydroxy-4-methoxyphenyl [f]	2	Plates (EtOH)	93	94 [h]

[a] Badcock, Cavill, Robertson, and Whalley, *J.*, 1950, 2961. [b] Chapman and Stephen, *J.*, 1923, **123**, 404. [c] Bhumgara, Desai, and Waravdekar, *Proc. Indian Acad. Sci.*, 1947, **25**, *A*, 322. [d] Joshi and Venkataraman, *J.*, 1934, 513. [e] Ref. 3. [f] Ref. 2. [g] Ballio and Pocchiari, *Gazzetta*, 1949, **79**, 913. [h] Bargellini and Martegiani, *Atti R. Accad. Lincei*, 1911, **20**, 183.

Benzyl 2-Hydroxy-5-methoxyphenyl Ketone.—A mixture of aluminium chloride (50 g.), *p*-dimethoxybenzene (24 g.), phenylacetyl chloride (24 g.), and ether (200 ml.) was refluxed for 8 hr. Material insoluble in ether was heated for 30 min. with 10% hydrochloric acid, and the product extracted with ether. The extract yielded to aqueous sodium hydroxide the required *deoxybenzoin* which crystallised from light petroleum (b. p. 40—60°) in yellow needles (16 g.), m. p. 45° (Found: C, 74·4; H, 5·8. $C_{15}H_{14}O_3$ requires C, 74·3; H, 5·8%). The ethanolic ferric colour was deep green. Ballio and Pocchiari [9] prepared this compound in a crude form but did not characterise it.

Synthesis of iso*Flavones* (*see Table* 3).—Normally the benzyl 2-hydroxyphenyl ketone (1 g.) was heated for 30—60 min. (A) with formamide (2—3 ml.) under reflux in nitrogen or (B) with formanilide (1·5 g.) at 250°. The product obtained with formamide was poured into

[6] Venkataraman, *Proc. Nat. Inst. Sci., India*, 1939, **5**, 255.
[7] O'Toole and Wheeler, *J.*, 1956, 4411.
[8] Baker, *J.*, 1933, 1381; Ollis and Weight, *J.*, 1952, 3826; Gupta and Seshadri, *J. Sci. Ind. Res., India*, 1957, **16**, *B*, 116.
[9] Ballio and Pocchiari, *Gazzetta*, 1949, **79**, 913.

TABLE 2. *New deoxybenzoins (benzyl phenyl ketones).*

Deoxybenzoin	Ketone from which prepared	Method (see above)	Form (solvent)	M. p.	Ethanolic Fe^{3+} colour	Found (%) C	H	N or S	Formula	Required (%) C	H	N or S
2-Benzoyloxyphenyl benzyl ketone	Benzyl 2-hydroxyphenyl [a]	3	Needles (EtOH)	94°	—	79·8	5·3	—	$C_{21}H_{16}O_3$	79·7	5·1	—
Benzyl 2-cinnamoyloxyphenyl ketone	,, ,,	3	Aggregates (EtOH)	99	—	80·8	5·5	—	$C_{23}H_{18}O_3$	80·7	5·3	—
Benzyl 2-hydroxy-4-*p*-nitrobenzoyloxyphenyl ketone	Benzyl 2 : 4-dihydroxyphenyl [b]	3	Yellow plates (EtOH)	178—180	Reddish-violet	67·0	4·2	3·6	$C_{21}H_{15}O_6N$	66·8	4·0	3·7
Benzyl 2-hydroxy-4-toluene-*p*-sulphonyloxyphenyl ketone	,, ,,	4	Needles (EtOH)	117	Red	66·4	4·7	8·2	$C_{21}H_{18}O_5S$	66·0	4·8	8·4
4-Benzoyloxy-2-hydroxyphenyl 4-methoxybenzyl ketone	2 : 4-Dihydroxyphenyl 4-methoxybenzyl [c]	5	Needles (AcOH and EtOH)	120—121	Red	73·1	5·1	—	$C_{22}H_{18}O_5$	72·9	5·0	—
2-Hydroxy-4-*p*-nitrobenzoyloxyphenyl 4-methoxybenzyl ketone	,, ,,	3	Yellow prisms (EtOH)	166—167	Red	65·2	4·5	3·2	$C_{22}H_{17}O_7N$	64·9	4·2	3·4
2-Hydroxy-4-toluene-*p*-sulphonyloxyphenyl 4-methoxybenzyl ketone	2 : 4-Dihydroxyphenyl 4-methoxybenzyl [c]	4	Prisms (EtOH)	91	Red	64·2	4·8	7·6	$C_{22}H_{20}O_6S$	64·1	4·9	7·8
2 : 4-Diacetoxyphenyl 4-nitrobenzyl ketone	2 : 4-Dihydroxyphenyl 4-nitrobenzyl [d]	1	Prisms (AcOH)	157—158	—	60·6	4·1	3·2	$C_{18}H_{15}O_7N$	60·5	4·2	3·9
2 : 4-Dibenzoyloxyphenyl 4-nitrobenzyl ketone	,, ,,	3	Yellow prisms (AcOH)	159—185°	—	70·6	3·7	2·5	$C_{28}H_{19}O_7N$	69·9	4·0	2·9
Benzyl 2-hydroxy-6-methoxyphenyl ketone	Benzyl 2 : 6-dihydroxyphenyl [f]	2	Needles (Aq. AcOH)	66	Green	73·8	5·9	(OMe 12·7)	$C_{15}H_{14}O_3$	74·3	5·8	(OMe, 12·8)
Benzyl 2 : 4 : 6-triacetoxyphenyl ketone [g]	Benzyl 2 : 4 : 6-trihydroxyphenyl [h]	1	Plates (Aq. AcOH)	125—126	—	64·9	5·0	—	$C_{20}H_{18}O_7$	64·9	4·9	—
Benzyl 2 : 4 : 6-tribenzoyloxyphenyl ketone	,, ,,	3	Prisms (Aq. AcOH)	175	—	75·6	4·1	—	$C_{35}H_{24}O_7$	75·5	4·4	—
4-Nitrobenzyl 2 : 4 : 6-triacetoxyphenyl ketone	4-Nitrobenzyl 2 : 4 : 6-trihydroxyphenyl [i]	1	Prisms (Aq. AcOH)	133—134	—	57·4	4·2	3·7	$C_{20}H_{17}O_9N$	57·8	4·1	3·4
4-Nitrobenzyl 2 : 4 : 6-tribenzoyloxyphenyl ketone	,, ,,	3	Needles (AcOH)	126—128	—	70·4	3·7	1·7	$C_{35}H_{23}O_9N$	70·0	3·8	2·3

[a] Chadha, Mahal, and Venkataraman, *J.*, 1933, 1459. [b] Ref. *a* of Table 1. [c] Baker and Eastwood, *J.*, 1929, 2897. [d] See Table 1. [e] Presumably decomposition occurred on melting. [f] Karmarkar, Shah, and Venkataraman, *Proc. Indian Acad. Sci.*, 1952, **36**, *A*, 552. [g] Gupta and Seshadri [8] state that this compound (m. p. 118—120°; no analysis) was obtained by the action of (1) acetic anhydride and perchloric acid or (2) acetyl chloride and pyridine on the corresponding trihydroxydeoxybenzoin; they mention that Mehta and Seshadri (*J.*, 1954, 3823) obtained by method 2 a compound with the same m. p. which was incorrectly formulated as 2 : 4 : 6-triacetoxyphenyl α-acetylbenzyl ketone. The analysis (C, 63·8; H, 5·1%) given by Mehta and Seshadri is not satisfactory for benzyl 2 : 4 : 6-triacetoxyphenyl ketone. [h] Ref. *b* of Table 1. [i] Ref. 3.

water. When formanilide was used the material was directly treated with an organic solvent. Purification was by crystallisation, in some instances after chromatography on alumina on which the unchanged deoxybenzoin was strongly adsorbed. Further details of some of the preparations are given below. The numbering refers to Table 3.

Nos. 7 *and* 8. Dearoylation occurred in these experiments. 7-Hydroxy*iso*flavone was extracted from a chloroform solution of the product by aqueous sodium hydroxide.

Nos. 10 *and* 14. The toluene-*p*-sulphonyl group was removed by refluxing the *iso*flavone produced with hydriodic acid in acetic anhydride as for demethylation. 7 : 4′-Dihydroxy*iso*flavone is the naturally occurring daidzein.

TABLE 3. iso*Flavones prepared by the action of formamide* (*A*) *or formanilide* (*B*) *on the corresponding benzyl* o-*hydroxyphenyl ketone. The order is that of increasing yield.*

No.	*iso*Flavone	Ketone from which prepared	Yield of *iso*flavone (%) A	B	Form (solvent)	M. p. and mixed m. p. unless otherwise stated
1	5 : 7-Dimethoxy-4′-nitro	2-Hydroxy-4 : 6-dimethoxyphenyl 4-nitrobenzyl [a]	15	25	Plates (C_6H_6)	220° [b]
2	7-Methoxy-4′-nitro	2-Hydroxy-4-methoxyphenyl 4-nitrobenzyl [a]	25	35	Needles ($COMe_2$)	245 [c]
3	7-Benzyloxy-3′ : 4′-methylenedioxy (*O*-benzyl-ψ-baptigenin)	4-Benzyloxy-2-hydroxyphenyl 3 : 4-methylenedioxybenzyl [d]	25	—	Needles (EtOH–AcOH)	168 [d]
4	*iso*Flavone	Benzyl 2-hydroxyphenyl [e]	30	—	Plates (EtOH)	132 [f]
5	7-Methoxy	Benzyl 2-hydroxy-4-methoxyphenyl [g]	30	—	Plates (MeOH)	155—156 [h]
6	7-Benzyloxy-4′-methoxy (*O*-benzylformononetin)	4-Benzyloxy-2-hydroxyphenyl 4-methoxybenzyl [d]	30	—	Plates (EtOH and EtOAc)	182 [d]
7	7-Hydroxy	4-Benzoyloxy-2-hydroxyphenyl benzyl [i]	—	40	Plates (Aq. AcOH)	208—210 [h]
8	,, ,,	Benzyl 2-hydroxy-4-*p*-nitrobenzoyloxyphenyl [j]	—	40	Plates (Aq. AcOH)	208—210 [h]
9	7-Benzyloxy	Benzyl 4-benzyloxy-2-hydroxyphenyl [h]	45	—	Plates) (EtOH)	171 [h]
10	4′-*Methoxy*-7-*toluene*-p-*sulphonyloxy*	2-Hydroxy-4-toluene-*p*-sulphonyloxyphenyl 4-methoxybenzyl [j]	—	50	Plates (C_6H_6)	168 [k]
11	6-Methoxy	Benzyl 2-hydroxy-5-methoxyphenyl [l]	—	50	Prisms ($COMe_2$ and AcOH)	174 [m]
12	7-Hydroxy-4′-methoxy (formononetin)	2-Hydroxy-4-*p*-nitrobenzoyloxyphenyl 4-methoxybenzyl [j]	—	50	Plates (Aq. AcOH)	253—254 [d]
13	,, ,,	4-Benzoyloxy-2-hydroxyphenyl 4-methoxybenzyl [j]	—	60	Plates (Aq. AcOH)	253—254 [d]
14	7-*Toluene*-p-*sulphonyloxy*	Benzyl 2-hydroxy-4-toluene-*p*-sulphonyloxyphenyl [j]	—	60	Needles	212—213 [n]

[a] See Table 1. [b] M. p. and m. p. of corresponding 4′-amino*iso*flavone in agreement with ref. 2. [c] Ref. 3. [d] Mahal, Rai, and Venkataraman, *J.*, 1934, 1769. [e] Ref. *a* of Table 2. [f] Authentic sample supplied by Professor J. Algar (Algar and McKenna, *Proc. Roy. Irish Acad.*, 1944, **49**, *B*, 225). [g] Ref. 4(*a*). [h] Mahal, Rai, and Venkataraman, *J.*, 1934, 1120. [i] Baker, ref. 8. [j] See Table 2. [k] New compound (Found: C, 65·8; H, 4·5; S, 7·4. $C_{23}H_{18}O_6S$ requires C, 65·4; H, 4·3; S, 7·6%). [l] See above after Table 2. [m] M. p.s of 6-methoxy-, 6-hydroxy-, and 6-acetoxy-*iso*flavone in agreement with m. p.s reported by Ballio and Pocchiari.[9] [n] New compound (Found: C, 67·3; H, 4·1; S, 8·0. $C_{22}H_{16}O_5S$ requires C, 67·3; H, 4·1; S, 8·2%); the *iso*flavone in sulphuric acid solution exhibited a blue fluorescence in ultraviolet light.

Nos. 12 *and* 13. Dearoylation occurred in these experiments.

The following deoxybenzoins did not yield *iso*flavones when heated with formamide or formanilide: benzyl 2-hydroxy-6-methoxyphenyl ketone (Table 2); benzyl 2-hydroxy-4 : 6-dimethoxyphenyl ketone;[10] benzyl 2-hydroxy-3 : 4-dimethoxyphenyl ketone;[9] benzyl

[10] Badcock, Cavill, Robertson, and Whalley, *J.*, 1950, 2961.

2-hydroxy-4 : 5-dimethoxyphenyl ketone (Table 1); benzyl 2-hydroxy-3 : 4 : 6-trimethoxyphenyl ketone.[9]

o-Hydroxyacetophenone when heated with benzamide in glycerol for 7 hr. at 250° gave flavone in 2% yield. No useful result was obtained when 2-hydroxy-4 : 6-dimethoxyphenyl 4-nitrobenzyl ketone (Table 1) and benzanilide were heated together at 250° for 30 min.

*2-Hydroxy-4-toluene-*p*-sulphonyloxyacetophenone*, which was obtained from resacetophenone by treatment with toluene-*p*-sulphonyl chloride and pyridine, separated from aqueous acetic acid in needles, m. p. 80—81° (Found: C, 58·8; H, 4·8; S, 10·4. $C_{15}H_{14}O_5S$ requires C, 58·7; H, 4·6; S, 10·4%). It did not give any identifiable compound when heated with formanilide.

The following 2-acyloxydeoxybenzoins (see Table 2) did not yield an *iso*flavone when heated: 2 : 4-dibenzoyloxyphenyl 4-nitrobenzyl ketone; benzyl 2 : 4 : 6-triacetoxyphenyl ketone; benzyl 2 : 4 : 6-tribenzoyloxyphenyl ketone; 4-nitrobenzyl 2 : 4 : 6-tribenzoyloxyphenyl ketone.

A mixture of 2-benzoyloxyphenyl benzyl ketone (Table 2) (0·7 g.) was heated in glycerol

TABLE 4. *2-Substituted* iso*flavones prepared by heating 2-acyloxydeoxybenzoins for 30 min. at 250°.*

*iso*Flavone	Ketone from which prepared	Yield of *iso*flavone (%)	Form (solvent)	M. p. and mixed m. p. unless otherwise stated
7-Benzoyloxy-2-phenyl	Benzyl 2 : 4-dibenzoyloxyphenyl [a]	8	Prisms (EtOH)	185—186° [b]
7-Acetoxy-2-methyl	Benzyl 2 : 4-diacetoxyphenyl [a]	40	Prisms (C_6H_6)	162 [c]
5 : 7-Diacetoxy-2-methyl-4′-nitro	4-Nitrobenzyl 2 : 4 : 6-triacetoxyphenyl [d]	50	Prisms (EtOH–$COMe_2$)	190 [e]
7-Acetoxy-2-methyl-4′-nitro	2 : 4-Diacetoxyphenyl 4-nitrobenzyl [d]	60	Needles ($COMe_2$)	245

[a] See Table 1. [b] Gupta and Seshadri.[3] [c] Baker and Robinson, *J.*, 1925, **127**, 1981. [d] See Table 2. [e] Dutta and Bose [3] give m. p. 190°. The diacetoxy*iso*flavone when deacetylated by treatment with sulphuric acid for 1 hr. at 0° gave 5 : 7-dihydroxy-2-methyl-4′-nitro*iso*flavone, m. p. and mixed m. p.[3] 260°. [f] Ref. 3.

(10 ml.) at 250° for 30 min. and the product was poured into water (100 ml.). 2-Phenyl*iso*flavone separated from dilute acetic acid in needles (0·4 g.), m. p. and mixed m. p.[11] 150°.

Benzyl 2-cinnamoyloxyphenyl ketone (Table 2) gave no useful result when heated in glycerol.

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UNIVERSITY COLLEGE, DUBLIN. [*Received, February 4th*, 1958.]

[11] Chadha, Mahal, and Venkataraman, *J.*, 1933, 1459.

XUM

510. *Photochemical Transformations. Part IV.* The Photochemistry of Prednisone Acetate.*

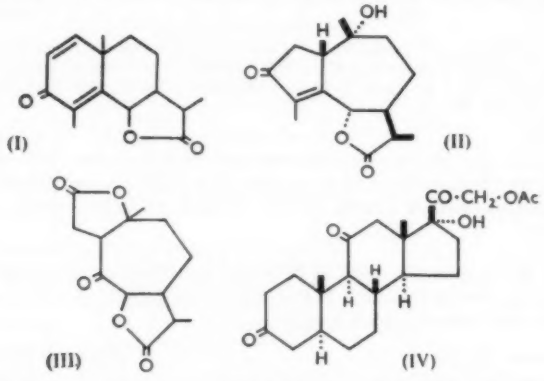
By D. H. R. Barton and W. C. Taylor.

Irradiation of prednisone acetate in aqueous acetic acid affords a product (VI) in which rings A and B have been changed into 5- and 7-membered respectively. Irradiation in ethanol at room temperature gives lumiprednisone acetate (VIII). In this compound ring A has become an umbellulone ring to which ring B is attached as a spiran. The chemistry of lumiprednisone acetate has been extensively explored. Irradiation in ethanol under more vigorous conditions furnishes a further isomer designated *neo*prednisone acetate (XXV). Irradiation in hot dioxan affords a "*para*" phenol.

The relation between lumiprednisone acetate and the other products formed by irradiation has been discussed and pertinent comparison made with the photochemistry of santonin.

Some of the results described in this paper have already been the subject of preliminary communications.[1]

The investigations described in this paper were initiated in parallel with our work on the photochemistry of santonin.[2,3,4] Some years ago we were led to suspect [5] that all *cyclo*hexadienones would prove to be readily capable of photochemical change. It was clearly desirable to examine, in particular, the effect of ultraviolet light on the medicinally important [6] prednisone acetate (V). Since it had been shown [2] that irradiation of santonin (I) in aqueous acetic acid afforded the lactone (II) our first experiments were concerned

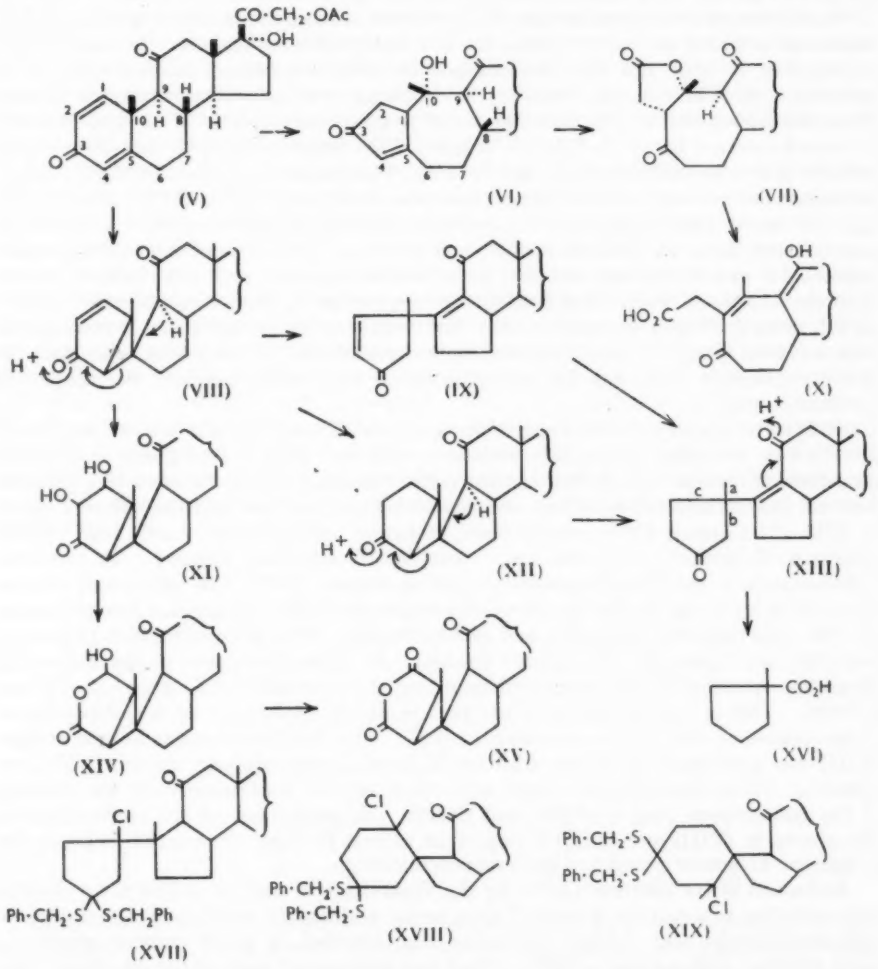


with the effect of these conditions on prednisone acetate (V). In this and subsequent photochemical experiments we showed that irradiation of 4 : 5α-dihydrocortisone acetate (IV) under the various conditions applied to prednisone acetate led to a fair recovery of unchanged material (IV). Any material not accounted for by recovery was shown to be an intractable mixture of products which could not be crystallised. We conclude that only ring A is involved in the photochemical reactions described in the sequel.

* Part III, *J.*, 1958, 688.

[1] Barton and Taylor, *Proc.*, 1957, 96, 147; *J. Amer. Chem. Soc.*, 1958, **80**, 244.
[2] Barton, de Mayo, and Shafiq, *J.*, 1957, 929.
[3] *Idem*, *Proc.*, 1957, 205; *J.*, 1958, 140.
[4] *Idem*, *Proc.*, 1957, 345; *J.*, 1958, in the press.
[5] Unpublished experiments in collaboration with Dr. E. L. Wheeler.
[6] Herzog, Payne, Jevnik, Gould, Shapiro, Oliveto, and Hershberg, *J. Amer. Chem. Soc.*, 1955, **77**, 4781; Nobile, Charney, Perlman, Herzog, Payne, Tully, Jevnik, and Hershberg, *ibid.*, p. 4184.

Irradiation of prednisone acetate (V) in refluxing aqueous acetic acid afforded a substance which is formulated as (VI) on the basis of analogy [2] and the following facts. The compound showed an ultraviolet maximum at 233 mμ (ε 15,500) characteristic of a *cyclo*pentenone (see below) with the degree of substitution indicated in formula (VI).[7] It gave infrared bands at 1740 (21-acetate), 1723 (20-ketone), 1685 (hydrogen-bonded



11-ketone and *cyclo*pentenone), and 1609 cm.$^{-1}$ (conjugated ethylenic linkage), and afforded a *cyclo*pentenone-derived mono-2 : 4-dinitrophenylhydrazone. It will be recalled that ozonolysis of the lactone (II) gave [2] the lactone (III). Similar ozonolysis of the irradiation product (VI) afforded a γ-lactone formulated as (VII). This derivative had bands in the infrared region at 1768 (γ-lactone), 1740 (21-acetate), and 1712 cm.$^{-1}$ (superimposed 11- and 20-ketones and the *cyclo*heptanone). It showed only low-intensity ketone absorption at 291 mμ in neutral solution, but in 0·1N-sodium hydroxide at room temperature it

[7] Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 76; Gillam and West, *J.*, 1942, 486.

at once gave a strong band at 440 mμ due to the anion of the acid (X). The compounds (IV), (V), and (VI) give no comparable band under the same conditions.

It has been shown [8] that the lactone (II) has the stereochemistry depicted. If, as already indicated, compound (VI) be assigned comparable stereochemistry, then it can be seen from models that the 11-ketone should be hydrogen-bonded with the tertiary 10-hydroxy group. The infrared evidence for this has been mentioned above.

Irradiation of prednisone acetate (V) in ethanol at room temperature under controlled conditions afforded an isomer which we call lumiprednisone acetate. This compound is sensitive to acid and base and cannot be chromatographed conveniently. It is formulated as (VIII) on the basis of the following evidence. The compound showed ultraviolet absorption at 218 and 265 mμ of a type characteristic of an umbellulone.[9] It showed infrared bands at 1735 (21-acetate), 1708 (superimposed 11- and 20-ketones), 1690 (ketone of umbellulone ring), and 1575 cm.$^{-1}$ (conjugated ethylenic linkage). Lumiprednisone acetate was readily hydrogenated to a dihydro-derivative (XII). This showed $\lambda_{max.}$ 207 mμ (ε 8100) indicative of a *cyclo*propane ring conjugated with a ketone.[9] It gave infrared bands at 1735 (21-acetate) and 1709 cm.$^{-1}$ (broad band representing superimposed 11- and 20-ketones and dihydroumbellulone ketone) and was stable to ozone. From these facts and from its composition this dihydro-derivative must contain an " extra " alicyclic ring indicated spectroscopically (see above) to be *cyclo*propane in conjugation with a ketone group. Lumiprednisone acetate contained 3 *C*-Me groups, one from the 21-acetate residue. The angular methyl group at $C_{(10)}$ must, therefore, be retained in the lumi-isomer.

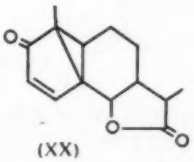
On brief treatment with acetic–perchloric acid or with Grade III alumina lumiprednisone acetate was converted into *iso*lumiprednisone acetate. This is formulated as (IX) for the following reasons. It showed an ultraviolet maximum at 241 mμ consistent with the presence (see further below) of two conjugated ketone functions and had infrared bands at 1735 (21-acetate), 1710 (superimposed 20-ketone and *cyclo*pentenone), 1675 (αβ-unsaturated 11-ketone), and 1585 cm.$^{-1}$ (conjugated ethylenic linkage). On catalytic hydrogenation it gave dihydro*iso*lumiprednisone acetate (XIII). In agreement with its formulation the latter showed an ultraviolet maximum at 251 mμ and had infrared bands at 1735 (superimposed 21-acetate and *cyclo*pentanone), 1673 (αβ-unsaturated 11-ketone) and 1595 cm.$^{-1}$ (conjugated ethylenic linkage). A subtraction curve of the ultraviolet absorption spectrum of this compound from that of its precursor (IX) gave $\lambda_{max.}$ 219 mμ (ε 7300). This is exactly the spectrum that would be expected [7] for a *cyclo*pentenone of the degree of substitution indicated in (IX). The dihydro*iso*lumiprednisone acetate (XIII) was also obtained by isomerisation of dihydrolumiprednisone acetate (XII) over alumina. These isomerisations under mild conditions are confirmatory for the presence of the *cyclo*propane ring in (VIII) and (XII). The mechanism of the rearrangements [see arrows in (VIII) and (XII)] is important in that it shows the relation between the 3- and the 11-ketone group and the *cyclo*propane ring.

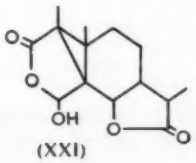
Reduction of the diketone (XIII) by the Wolff–Kishner method, followed by chromic acid oxidation in a current of steam,[10] gave acetic acid and, in small yield, 1-methyl*cyclo*pentanecarboxylic acid (XVI). The latter was identified by paper chromatography in three different systems (see p. 2508). That this represented part of the dihydro*iso*lumiprednisone acetate (XIII) molecule was confirmed by a control determination with **4** : 5α-dihydrocortisone acetate which gave only acetic acid, and by the following experiments. Dihydro*iso*lumiprednisone acetate (XIII) was treated with toluene-ω-thiol in the presence of dry hydrogen chloride to furnish in high yield a nicely crystalline product. This showed only benzylthio-absorption at 210 mμ (equivalent to two residues) and had infrared

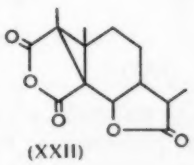
[8] Barton, *Proc.*, 1958, 61; Djerassi, Osiecki, and Herz, *J. Org. Chem.*, 1957, **22**, 1361.
[9] Eastman, *J. Amer. Chem. Soc.*, 1954, **76**, 4115, and references there cited.
[10] Pregl, " Quantitative Organic Microanalysis," ed. J. Grant, J. and A. Churchill Ltd., London, 5th edn., 1951, p. 206.

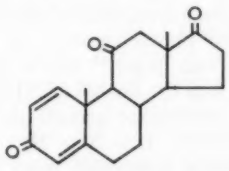
bands (in Nujol) at 1725 (21-acetate) and 1710 cm.$^{-1}$ (superimposed 11- and 20-ketones). In composition this substance represented the conversion of the *cyclo*pentanone of (XIII) into the thioketal (confirmed by a negative Zimmermann test and by the diminution of the intensity of the infrared band at about 1730 cm.$^{-1}$) with addition of one mol. of hydrogen chloride. The loss of the αβ-unsaturated 11-ketone and the addition of chloride could be explained as in (XIII; see arrows). However, the dithioketal did not give an αβ-unsaturated ketone with hot pyridine and therefore cannot be a β-chloro-ketone (with α-hydrogen). The formation of this compound is best explained by migration of bonds (a), (b), or (c) in (XIII) to give respectively the compounds (XVII), (XVIII), and (XIX), one of which formulæ must represent our product. Removal of the dithioketal grouping with Raney nickel (spectrophotometric control), followed by chromic acid oxidation, gave no trace of 1-methyl*cyclo*pentanecarboxylic acid.

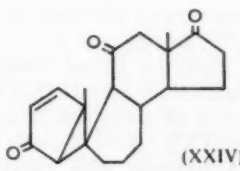
During the work [3,11] on lumisantonin (XX) the umbellulone ring was hydroxylated with osmium tetroxide and the product cleaved with periodic acid to furnish the neutral lactol (XXI). On further oxidation with chromic acid this gave [3] the anhydride (XXII), showing infrared bands at 1830 and 1770 cm.$^{-1}$. Treatment of lumiprednisone acetate in the same way gave the glycol (XI) showing ultraviolet absorption at 210 mμ (conjugated ketone and *cyclo*propane ring; cf. above) and infrared bands (in Nujol) at 1739 (21-acetate) and 1712 cm.$^{-1}$ (superimposed 11- and 20-ketones and dihydroumbellulone ketone). This was cleaved by periodic acid to afford the neutral lactol (XIV). This had no ultraviolet absorption but showed infrared bands (in Nujol) at 1767 (γ-lactol), 1748 (21-acetate), 1727 (20-ketone), and 1716 cm.$^{-1}$ (11-ketone). The lactol rapidly consumed one " atom " of oxygen on chromic acid oxidation under conditions where 4 : 5α-dihydrocortisone acetate (IV) showed no significant uptake. Although the product did not crystallise it was clearly the anhydride (XV), as shown by infrared bands at 1853 and 1773 [see bands for (XXII) mentioned above], 1745 (21-acetate), and 1718 cm.$^{-1}$ (superimposed 11- and 20-ketones).


(XX)


(XXI)


(XXII)


(XXIII)


(XXIV)

The photochemical isomerisation of prednisone acetate (V) to the lumi-isomer (VIII) is probably a general reaction of 11-keto-steroids with the dienone system in ring A. Thus androsta-1 : 4-diene-3 : 11 : 17-trione (XXIII), prepared by oxidation of prednisone with sodium bismuthate,[12,13] was isomerised readily to a lumi-isomer which we formulate, on the basis of its spectroscopic properties and optical rotation, as (XXIV).

Chromatography of the mother-liquors remaining after removal of lumiprednisone acetate afforded, besides unchanged prednisone acetate, a further isomer which we call *neo*prednisone acetate. This was obtained in only minute yield, but irradiation of

[11] Arigoni, Bosshard, Bruderer, Büchi, Jeger, and Krebaum, *Helv. Chim. Acta*, 1957 **40** 1732; see also Cocker, Crowley, Edward, McMurry, and Stuart, *J.*, 1957, 3416.
[12] Rigby, *J.*, 1950, 1907.
[13] Brooks and Norymberski, *Biochem. J.*, 1953, **55**, 371.

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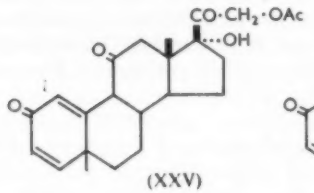
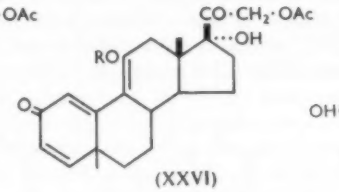
prednisone acetate in refluxing ethanol under controlled conditions improved the ease of preparation and gave sufficient material for our purposes. The compound had an ultraviolet absorption spectrum essentially the same as that of prednisone acetate. The infrared bands in the carbonyl (and hydroxy) region were superimposable upon those of prednisone acetate. Clearly *neo*prednisone acetate is a homoannular *cyclo*hexadienone. We formulate it as (XXV) on the basis of this and the following evidence. The ultraviolet spectrum of prednisone acetate is the same in ethanol and in 0·1N-ethanolic sodium hydroxide. *neo*Prednisone acetate gives an immediate red-brown colour on dissolution in this 0·1N-base and shows a strong band at 468 mμ which we assign to the anion of the enol (XXVI; R = H). On acidification this band shifts reversibly to 340 mμ, which is the position to be expected for the enol (XXVI; R = H). By very brief treatment with 0·1N-methanolic sodium hydroxide followed by acidification it was possible to isolate the enol in crystalline form. It showed the same spectroscopic behaviour as detailed above and showed infrared bands at 1735 (21-acetate), 1720 (20-ketone), 1660 (3-ketone), and 1605 cm.$^{-1}$ (conjugated ethylenic linkage). The saturated 11-ketone band of the diketone (XXV) had thus been destroyed by enolisation, as already formulated in (XXVI). Acetylation of the enol with pyridine–acetic anhydride gave the expected enol acetate (XXVI; R = Ac). This had ultraviolet absorption at 242 and 288 mμ in agreement with this formulation and showed infrared bands at 1749 (11-enol acetate), 1733 (21-acetate), 1662 (3-ketone), and 1621 and 1605 cm.$^{-1}$ (conjugated ethylenic linkages).

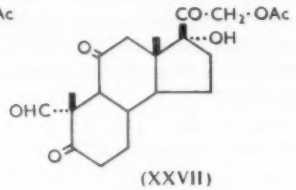
During the examination of *neo*prednisone acetate we had occasion to ozonise prednisone acetate in ethyl acetate at low temperature under spectroscopic control. This gave in



(XXV)



(XXVI)



(XXVII)

satisfactory yield the aldehyde (XXVII), which had infrared bands at 2725 (aldehyde-hydrogen), 1733 (superimposed aldehyde and 21-acetate), and 1701 cm.$^{-1}$ (superimposed 5- and 11-ketones), in agreement with the assigned constitution.

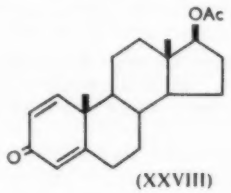
The photochemical conversion of a dienone into a phenol was first effected by Staudinger and Bereza.[14] During our work on the photochemistry of prednisone acetate there appeared a paper by Dutler, Bosshard, and Jeger[15] which reported the conversion of 1-dehydrotestosterone acetate (XXVIII) into the phenol (XXIX) by irradiation in dioxan. The application of these conditions to prednisone acetate gave us a phenol which we formulate as (XXX; R = X = H) or (XXXI; R = X = H) on the basis of the following evidence. Acetylation with pyridine–acetic anhydride gave a monoacetate (XXX or XXXI; R = Ac, X = H). The phenol and its acetate had the expected spectroscopic properties (see p. 2509). On bromination in aqueous dioxan in the presence of calcium carbonate with excess of bromine the phenol gave only a monobromo-derivative (XXX or XXXI; R = H, X = Br). Under the same conditions the phenol (XXXII; R = X = H) * gave a dibromo-derivative (XXXII; R = H, X = Br) isolated, after treatment with pyridine–acetic anhydride, as the diacetate (XXXII; R = Ac, X = Br). These experiments suggest that the phenol from prednisone acetate is of the "*para*" type,

* This phenol was very kindly provided by Messrs. Glaxo Laboratories Ltd. It is our understanding that this substance and many of its derivatives will be described in a paper to be submitted shortly for publication in this *Journal*.

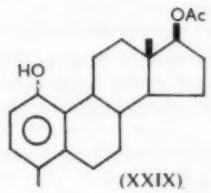
[14] Staudinger and Bereza, *Annalen*, 1911, **380**, 243.
[15] Dutler, Bosshard, and Jeger, *Helv. Chim. Acta*, 1957, **40**, 494.

as are (XXX) and (XXXI), and not of the "*meta*" type such as (XXXII). Inspection of infrared data (see p. 2509) confirmed this.

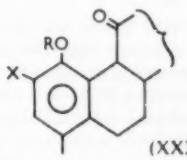
Lumiprednisone acetate probably occupies a special position in the photochemical transformation products of prednisone acetate. Thus (see XXXIII) further irradiation could well promote the migration of bond (a) or (b) to $C_{(10)}$ with re-formation of the *cyclo*hexadienone system. In the first case prednisone acetate is re-formed, in the second *neo*prednisone



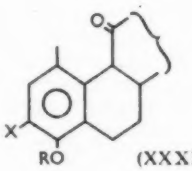
(XXVIII)



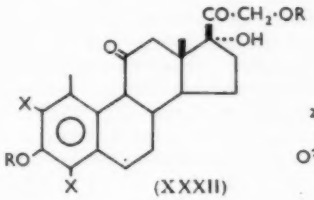
(XXIX)



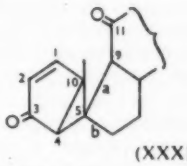
(XXX)



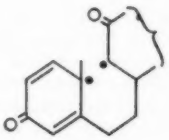
(XXXI)



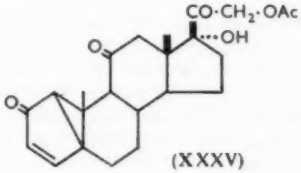
(XXXII)



(XXXIII)



(XXXIV)



(XXXV)

acetate results. Migration of bond (a), on the other hand, to $C_{(4)}$ would give the "*para*" phenol of type (XXX), whilst similar migration of bond (b) would give a "*para*" phenol of type (XXXI). We have confirmed that lumiprednisone acetate does not rearrange to a phenol when merely refluxed in dioxan, but does furnish the phenol (XXX or XXXI; R = X = H) mentioned above on irradiation in refluxing dioxan.

The compound "A4" of Dutler, Bosshard, and Jeger[15] may, on the basis of its ultraviolet absorption spectrum, have a structure comparable with that of our lumiprednisone acetate. However, the $[M]_D$ change for making "A4" is strongly positive, whereas the $[M]_D$ change for the conversion of prednisone into lumiprednisone acetate is strongly negative. If the compounds are indeed comparable then they may well differ in stereochemistry. We do not wish to imply any stereochemical assignments for the prednisone acetate derivatives described in the present paper.

The formation of substantially one product, lumiprednisone acetate, on irradiation of prednisone acetate in ethanol contrasts with the multiplicity of products reported by Dutler, Bosshard, and Jeger[15] from the irradiation of 1-dehydrotesterone acetate in dioxan. We believe that this is probably not a solvent effect but a consequence of the presence of the 11-keto-group in prednisone acetate. This must undoubtedly weaken the 9 : 10-bond because the diradical formed by homolytic rupture (see XXXIV) would be stabilised not only as a $C_{(10)}$ phenoxide radical but also by resonance of the $C_{(9)}$-radical with the 11-ketone. It is understandable therefore why lumiprednisone is formed by migration of the 9 : 10-bond rather than by internal rearrangement of the *cyclo*hexadienone ring (1 : 5-bond formation) such as happens preferentially in santonin[3,11] and (presumably) in 1-dehydrotestosterone acetate.

XUM

Lumiprednisone acetate is ***not*** the precursor of the *cyclo*pentenone (VI). Thus, whilst lumisantonin (XX)[3,11] is smoothly transformed into (II) in refluxing aqueous acetic acid,[3] lumiprednisone acetate is stable under these conditions. Indeed, the product (VI) could be derived from an isomer of prednisone acetate formulated as in (XXXV), which we have not isolated as a stable product, although there is probably a direct route to (VI) from (V) of the type encountered in santonin chemistry.[3]

Experimental

M. p.s were taken on the Kofler block. Ultraviolet absorption spectra were determined for EtOH solutions with the Unicam S.P. 500 Spectrophotometer. All rotations are in $CHCl_3$. Infrared spectra also refer to $CHCl_3$ solution unless stated otherwise. Light petroleum refers to the fraction of b. p. 60—80°.

Irradiation in Aqueous Acetic Acid.—Prednisone acetate (3·1 g.) in 45 : 55 acetic acid–water (250 ml.) was irradiated in a quartz flask under reflux with a bare mercury arc (125 w) lamp until the rotation fell to approx. 130° (about 1 hr.). Removal of the solvent under reduced pressure afforded a gum which was separated (sodium hydrogen carbonate) into neutral and acidic fractions. The neutral fraction (2·9 g.) was chromatographed over silica gel (150 g.): elution with chloroform (3 fractions) yielded starting material (0·45 g.); elution with acetone–chloroform (1 : 4) afforded the *acetate* (VI) (0·40 g.), prisms (from methanol), m. p. 240—243°, $[\alpha]_D$ +134° (*c* 0·51), $\lambda_{max.}$ 233 mμ (ε 15,500), $\nu_{max.}$ 1740, 1723, 1685, and 1609 cm.$^{-1}$ (Found: C, 66·0; H, 7·4; Ac, 10·7. $C_{23}H_{30}O_7$ requires C, 66·0; H, 7·25; 1Ac, 10·4%). The 2 : 4-*dinitrophenylhydrazone* (from chloroform–ethanol) had m. p. 270—275° (decomp.), $\lambda_{max.}$ 390—392 mμ (ε 29,500) (Found: C, 58·0; H, 6·0; N, 9·4. $C_{29}H_{34}O_{10}N_4$ requires C, 58·2; H, 5·7; N, 9·35%).

Ozonolysis of the Acetate (VI).—The acetate (40 mg.) in chloroform (15 ml.) was ozonised at −70° for 18 min. (disappearance of ultraviolet max. at 233 mμ). The ozonide was decomposed by evaporation of the solvent on the steam-bath in the presence of water (2 ml.); separation of the mixture through sodium hydrogen carbonate yielded a neutral fraction (20 mg.) which was crystallised from methanol (plates) to give the *lactone* (VII), m. p. 143—145°, $[\alpha]_D$ +128° (*c* 0·66), $\lambda_{max.}$ 291 mμ (ε 200), $\lambda_{max.}$ (in 0·1N-NaOH) 439—442 mμ (ε 8000), $\nu_{max.}$ 3420, 1768, 1740, and 1712 cm.$^{-1}$ (Found: C, 62·6; H, 6·6. $C_{22}H_{28}O_8$ requires C, 62·8; H, 6·7%).

Irradiation of 4 : 5α-*Dihydrocortisone Acetate.*—(*a*) 4 : 5α-Dihydrocortisone acetate (880 mg.) in 45 : 55 acetic acid–water (200 ml.) (initial $[\alpha]_D$ +110°) was irradiated as described above for 3 hr. (final $[\alpha]_D$ +65°). Separation of the product through sodium hydrogen carbonate yielded a neutral fraction (540 mg.), which was chromatographed on alumina (Grade V; 100 g.) (elution with benzene and 8 : 1-benzene–ethyl acetate) to yield starting material (490 mg.) (m. p. and mixed m. p., $[\alpha]_D$, and infrared spectrum) as the only isolable product. The acidic fraction (330 mg.) was a dark gum which did not afford any crystalline material on chromatography over silica gel.

(*b*) 4 : 5α-Dihydrocortisone acetate (860 mg.) in ethanol (200 ml.) (initial $[\alpha]_D$ +110°) was irradiated under reflux for 1 hr. (final $[\alpha]_D$ +92°). Starting material (553 mg.) (m. p. and mixed m. p., $[\alpha]_D$, and infrared spectrum) was recovered by crystallisation; the remaining material was a non-crystallisable syrup.

(*c*) 4 : 5α-Dihydrocortisone acetate (730 mg.) in dioxan (100 ml.) was irradiated under reflux for 1 hr. ($[\alpha]_D$ changed from +110° to +81°). Chromatography of the product over alumina afforded starting material (480 mg.) (m. p., mixed m. p., $[\alpha]_D$, and infrared spectrum).

(*d*) 4 : 5α-Dihydrocortisone acetate (867 mg.) in dioxan (50 ml.) diluted with ethanol (300 ml.) was irradiated at room temperature for 30 hr. (rotation changed from +110° to +100°). Chromatography of the product on alumina afforded starting material (735 mg.) (m. p. and mixed m. p., $[\alpha]_D$, and infrared spectrum).

Lumiprednisone Acetate.—Prednisone acetate (3·4 g.) in ethanol (350 ml.) was irradiated in a quartz flask at room temperature (air cooling) until the rotation fell to approx. 0° (about 20 hr.). Removal of the solvent under reduced pressure afforded a yellow gum which was fractionally crystallised from ethyl acetate–light petroleum to constant rotation, giving as the less soluble product, *lumiprednisone acetate* (VIII) (0·8 g.), plates (from methanol), m. p. 224—226°, $[\alpha]_D$ −84° (*c* 0·80), $\lambda_{max.}$ 218 and 265 mμ (ε 5900 and 2300 respectively), $\nu_{max.}$ 1735, 1708, 1690, and 1575 cm.$^{-1}$ [Found: C, 68·95; H, 7·05; *C*-Me, 9·5. $C_{23}H_{28}O_6$ requires C, 69·0;

H, 7·05; 3*C*-Me (1 from 21-acetate), 11·3%]. Starting material (540 mg.) was obtained as the more soluble fraction. Chromatography of the mother-liquors over silica gel (100 g.) and elution with benzene–chloroform (1 : 1) gave a fraction which was chromatographed on alumina (Grade V; 20 g.) to give, after elution with benzene–chloroform (4 : 1), *neo*prednisone acetate (7 mg.).

Dihydrolumiprednisone Acetate.—Lumiprednisone acetate in ethanol was hydrogenated over palladium–charcoal (10%) (rapid uptake of 1 mol.). The *dihydro*-derivative (XII), prisms or needles (from ethyl acetate–light petroleum), had m. p. 200—203°, $[\alpha]_D$ +95° (*c* 1·15), $\lambda_{max.}$ 207 mμ (ε 8100), $\nu_{max.}$ 1735 and 1709 (broad) cm.$^{-1}$ (Found: C, 68·8; H, 7·65. $C_{23}H_{30}O_6$ requires C, 68·6; H, 7·5%). The compound was recovered unchanged (m. p. and mixed m. p.) after treatment for 30 min. at −70° with 3 molar equivalents of ozone.

iso*Lumiprednisone Acetate.*—(*a*) Lumiprednisone acetate (300 mg.) in acetic acid (25 ml.) and 70% perchloric acid (0·05 ml.) was heated at 85° for 20 min. The solution was then concentrated *in vacuo* to about 5 ml., diluted with ethyl acetate, and worked up the usual way, to yield iso*lumiprednisone acetate* (IX) (211 mg.), blades (from ethyl acetate–light petroleum), m. p. 202—204° (after loss of solvent at 140°), $[\alpha]_D$ −103° (*c* 0·50), $\lambda_{max.}$ 210 and 241 mμ (ε 8000 and 10,600 respectively), $\nu_{max.}$ 1735, 1710, 1675, and 1585 cm.$^{-1}$ [Found: C, 68·8; H, 6·85; *C*-Me, 11·9. $C_{23}H_{28}O_6$ requires C, 69·0; H, 7·05; 3*C*-Me (1 from 21-acetate), 11·3%].

(*b*) Lumiprednisone acetate (42 mg.) in benzene–chloroform (7 : 3) (30 ml.) was shaken with alumina (Grade III; 90 mg.) for 1 hr. The mixture was filtered, the alumina was washed 3 times with warm methanol, and the combined filtrates were evaporated to yield *iso*lumiprednisone acetate (9 mg.).

(*c*) Lumiprednisone acetate was recovered unchanged (m. p., mixed m. p., and $[\alpha]_D$) after 12 hours' refluxing in acetic acid–water (45 : 55).

*Dihydroiso*lumiprednisone *Acetate.*—*iso*Lumiprednisone acetate in ethanol was hydrogenated on palladium–charcoal (10%) (rapid uptake of 1 mol.). The *dihydro*-derivative (XIII) formed needles (from ethyl acetate–ether–light petroleum), m. p. 192—195°, $[\alpha]_D$ +127° (*c* 0·50), $\lambda_{max.}$ 251 mμ (ε 8700), $\nu_{max.}$ 1735, 1673, and 1595 cm.$^{-1}$ (Found: C, 68·6; H, 7·35. $C_{23}H_{30}O_6$ requires C, 68·6; H, 7·5%). The *monosemicarbazone*, prepared in aqueous ethanol at room temperature, had m. p. 253—256°, $\lambda_{max.}$ 236 mμ (ε 15,200), $\nu_{max.}$ 1740, 1720, 1690, 1655, and 1577 cm.$^{-1}$ (Found: N, 8·85. $C_{24}H_{33}O_6N_3$ requires N, 9·15%). The compound gave a negative Zimmermann test in agreement with the disappearance of the *cyclo*pentanone carbonyl absorption from the infrared spectrum.

Isolation and Characterisation of 1-*Methyl*cyclo*pentanecarboxylic Acid.*[16]—Dihydro*iso*lumiprednisone acetate (330 mg.) and hydrazine hydrate (0·2 ml.) were refluxed in ethanol (2 ml.) for 2 hr.; sodium (0·3 g.) in ethanol (5 ml.) was added, and the mixture heated at 150° for 7 hr. The crude product obtained after being worked up in the usual way gave a negative Zimmermann test; in the infrared spectrum, the comparative weakness of the carbonyl bands (1690, 1663 cm.$^{-1}$) suggested that considerable reduction had occurred also at the 11- and the 20-carbonyl position. This was not overcome by reduction of the semicarbazone under rigidly anhydrous conditions, the product being essentially the parent ketone (infrared spectrum and positive Zimmermann test).

Oxidation of the Wolff–Kishner reduction product was conducted under similar conditions to those described by Pregl [10] for the determination of *C*-methyl. The crude reduction product (*ca.* 100 mg.) was introduced into the reaction flask containing chromic acid reagent (10 ml.) (containing 10 times the concentration of chromium trioxide detailed in ref. 10) and concentrated sulphuric acid (2 ml.); the mixture was brought rapidly to the boil and water slowly distilled off, water being introduced at an equivalent rate to maintain a constant volume in the flask. Distillation was continued until production of volatile acid ceased (titration of distillates). The alkaline distillates were evaporated to dryness and acidified with the minimum volume of 6N-sulphuric acid, and the solution was extracted with ether (5 × 3 ml.). The combined ether extracts were dried (Na_2SO_4) and then carefully evaporated to dryness; the residue was subjected to partition chromatography on aqueous silica gel, with chloroform–butanol as the mobile phase,[17] the eluates being titrimetrically estimated for acids with 0·05N-sodium hydroxide and thymol-blue as indicator. Control experiments showed that 1-methyl*cyclo*pentanecarboxylic was quantitatively recovered under the conditions of oxidation and that it could

[16] Meerwein, *Annalen*, 1918, **417**, 255.
[17] Elsdon, *Biochem. J.*, 1946, **40**, 252.

XUM

be quantitatively separated from acetic acid by the partition chromatography, being eluted with water-saturated chloroform containing 1% (v/v) of butan-1-ol (CB1); acetic acid was eluted (94% recovery) with 20% butan-1-ol–chloroform (CB20). In a typical oxidation 99·4 mg. of crude reduction product afforded volatile acid equivalent to 11·82 ml. of 0·05N-alkali (2 mol. of acid require approx. 14 ml.). The concentrated volatile acid fraction, which gave spots on paper chromatograms with R_F values (in butan-1-ol–1·5N-ammonia) of 0·06 (acetic acid) and 0·43, was partitioned on a silica gel column (7 g.). Elution with CB1 (10 ml.) gave a fraction which consumed 0·098 ml. of 0·05N-alkali; isolation of the acidic material afforded a concentrate containing 1-methyl*cyclo*pentanecarboxylic acid, identified by paper chromatography in 3 solvent systems:

	R_F values		
	Oxidation product	1-Methyl*cyclo*pentanecarboxylic acid	1-Methyl*cyclo*hexanecarboxylic acid
*iso*Propanol–0·15N-ammonia	0·89	0·89	—
Butan-1-ol–1·5N-ammonia	0·43	0·43	0·52
Ethanol (95%)–1% ammonia	0·63	0·63	—

Elution with CB20 yielded acetic acid (R_F 0·06) equivalent to 10·32 ml. of 0·05N-alkali.

4 : 5α-Dihydrocortisone acetate (93 mg.), oxidised in a similar fashion, yielded acetic acid as the only detectable volatile acid.

*Reaction of Dihydroiso*lumiprednisone *Acetate with Toluene-ω-thiol.*—Dihydro*iso*lumiprednisone acetate (267 mg.) in acetic acid (3 ml.) saturated with hydrogen chloride was treated at 0° with toluene-ω-thiol (0·16 ml., 1 mol.); separation of crystalline product commenced after 30 min. After 2 hr. the mixture was carefully neutralised with sodium hydrogen carbonate, and extracted with chloroform to give the derivative [(XVII), (XVIII), or (XIX)], plates (from methanol), m. p. 172—173°, $\lambda_{max.}$ 210 mμ (ε 24,000), $\nu_{max.}$ (Nujol) 1725 and 1710 cm.$^{-1}$ (Found: C, 66·4; H, 6·7; Cl, 5·25; S, 9·55. $C_{37}H_{45}O_5S_2Cl$ requires C, 66·4; H, 6·8; Cl, 5·3; S, 9·6%). The compound gave a positive Beilstein test for halogen and a negative Zimmermann test; there was no αβ-unsaturated ketone chromophore (ultraviolet spectrum) after treatment with pyridine at 100°. The mercaptal (230 mg.) in dioxan (5 ml.) was refluxed with Raney nickel for 12 hr. (disappearance of ultraviolet max. at 215 mμ). Oxidation of the crude product yielded no 1-methyl*cyclo*pentanecarboxylic acid (paper chromatography).

Hydroxylation of Lumiprednisone Acetate.—Reaction of lumiprednisone acetate (36·4 mg.) with osmium tetroxide (23 mg.) for 48 hr. and decomposition of the osmate ester with hydrogen sulphide afforded the *glycol* (XI), prisms (from ethyl acetate–light petroleum), m. p. 225—228°, $[\alpha]_D$ +120° (*c* 0·70), $\lambda_{max.}$ 210 mμ (ε 7300), $\nu_{max.}$ (Nujol) 1739 and 1712 cm.$^{-1}$ (Found: C, 63·6; H, 7·05. $C_{23}H_{36}O_8$ requires C, 63·6; H, 6·95%).

The glycol (in aqueous ethanol) was cleaved by sodium metaperiodate (rapid uptake of 2 mol.) to furnish the *lactol* (XIV), leaflets from ethyl acetate–methanol–light petroleum, m. p. 211—214°, $[\alpha]_D$ +136° (*c* 0·50), high-intensity ultraviolet maximum, and bands in the infrared (Nujol) at 1767, 1748, 1727, and 1716 cm.$^{-1}$ (Found: C, 62·65; H, 6·7. $C_{22}H_{28}O_8$ requires C, 62·8; H, 6·7%).

Oxidation of the Lactol (XIV).—The lactol was oxidised rapidly with the chromic acid–acetone reagent [18] to give a product which did not crystallise; a purified fraction obtained by chromatography on silica gel (elution with 4 : 1 benzene–ethyl acetate) had strong infrared bands at 1853 and 1773 (5-membered unsaturated anhydride), 1745 (21-acetate), and 1718 cm.$^{-1}$ (11- and 20-ketones). The lactol had consumed 0·75 equivalent of oxygen after 24 hr. in acetic acid–sodium dichromate; a control experiment showed that 4 : 5α-dihydrocortisone acetate consumed 0·09 equivalent of oxygen in the same period.

Isomerisation of Dihydrolumiprednisone Acetate.—Dihydrolumiprednisone acetate (40 mg.) was chromatographed on alumina (Grade III; 6 g.) (larger quantities of alumina gave poor recovery of material); elution with benzene–ethyl acetate (85 : 15 and 80 : 20; 8 × 50 ml. fractions) gave material enriched in dihydro*iso*lumiprednisone acetate ($\varepsilon_{251}/\varepsilon_{210}$ ~1—1·5; cf. 2·9 for the pure compound). These fractions were combined (15 mg.) and rechromatographed on alumina (Grade III; 5·5 g.); material eluted with benzene–ethyl acetate (88 : 12, 2 fractions; and 86 : 14, 2 fractions) was recrystallised 3 times from ethyl acetate–light petroleum, to give dihydro*iso*lumiprednisone acetate (3·5 mg.), m. p. and mixed m. p. 193—195°,

[18] Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.

$\lambda_{max.}$ 251 mμ (ε 8700). The semicarbazone had m. p. 253—255°, undepressed on admixture with dihydro*iso*lumiprednisone acetate semicarbazone.

Irradiation of Prednisone Acetate in Dioxan.—Prednisone acetate (1·4 g.) in dioxan (100 ml.) was irradiated in a quartz flask under reflux until the rotation fell to approx. 100° (about 1·3 hr.). Chromatography of the product on silica gel (20 g.) and elution with benzene–chloroform (70 : 30) yielded a fraction (530 mg.) from which were separated by chromatography on alumina (Grade V, 30 g.) starting material (120 mg.) and *iso*lumiprednisone acetate (25 mg.); elution with benzene–chloroform (6 : 4) afforded the *phenol* (XXX or XXXI; R = X = H) (200 mg.), needles (from methanol), m. p. 258—265° (decomp.), $[\alpha]_D$ +294° (*c* 1·20 in dioxan), $\lambda_{max.}$ 210 and 286 mμ (ε 21,600 and 3300 respectively), $\lambda_{max.}$ in 0·1N-NaOH 220, 246, and 302 mμ (ε 33,500, 11,500, and 4200 respectively) (Found: C, 69·3; H, 6·65. $C_{23}H_{28}O_6$ requires C, 69·0; H, 7·05%). The *acetate*, prepared in acetic anhydride–pyridine overnight, had m. p. 223—227° (from methanol), $[\alpha]_D$ +296° (*c* 1·05 in dioxan), $\lambda_{max.}$ 220 and 268 mμ (ε 7300 and 520 respectively) (Found: C, 68·2; H, 6·9; Ac, 19·0. $C_{25}H_{30}O_7$ requires C, 67·85; H, 6·8; 2Ac, 19·45%).

The *bromo-derivative* was prepared in aqueous dioxan (1 : 8) in the presence of calcium carbonate (uptake of 1 mol.); it had m. p. 235—238° (from ethyl acetate–light petroleum), $\nu_{max.}$ 3521, 3460 (hydrogen-bonded phenolic hydroxyl), 3401 (hydroxyl), 865 cm.$^{-1}$ (Found: C, 57·2; H, 5·95; Br, 16·9. $C_{23}H_{27}O_6Br$ requires C, 57·6; H, 5·7; Br, 16·7%).

A solution of the phenol (XXXII; R = X = H) (27·2 mg.) in dioxan (3 ml.) and water (0·1 ml.) was titrated in presence of calcium carbonate (500 mg.) with bromine in dioxan (2 mol. uptake). Inorganic material was removed and the filtrate diluted with water (8 ml.) and worked up in the usual way with ethyl acetate. Acetylation of the crude product in pyridine–acetic anhydride overnight afforded the *acetate* (XXXII; R = Ac; X = Br) (11 mg.), m. p. 215—217° (from ethyl acetate–light petroleum), with no strong bands in the infrared spectrum (Nujol) in the 800—900 cm.$^{-1}$ region (Found: Br, 26·9. $C_{25}H_{28}O_7Br_2$ requires Br, 26·6%). Under similar conditions of bromination, 4 : 5α-dihydrocortisone acetate was recovered unchanged.

Infrared Spectra of the Phenols and Derivatives in the 800—900 cm.$^{-1}$ Region of the Spectrum.—All spectra were taken (for solubility reasons) in Nujol with the results summarised in the annexed Table.

Compound	Intense band (cm.$^{-1}$)	Substitution assignment.[19, 20]
(XXX or XXXI; R = X = H)	809	1 : 2 : 3 : 4-
(XXX or XXXI; R = Ac, X = H)	817	1 : 2 : 3 : 4-
(XXX or XXXI; R = Ac, X = Br)	865	1 : 2 : 3 : 4 : 5-
(XXXII; R = Ac, X = H and Ac at 17)	865	1 : 2 : 3 : 5-
(XXXII; R = Ac, X = Br)	None	1 : 2 : 3 : 4 : 5 : 6-

All compounds showed, in addition, a weak band at 844—847 cm.$^{-1}$ which was independent of the substitution pattern.

Irradiation of Lumiprednisone Acetate.—Lumiprednisone acetate (80 mg.) in dioxan (10 ml.) was irradiated in a quartz tube under reflux until the rotation rose to approx. +150° (7 min.). Starting material (10 mg.) and oil were separated (more soluble fraction) by crystallisation of the product from ethyl acetate; the remaining material was chromatographed on silica gel (20 g.). The material eluted with benzene–ethyl acetate (92 : 8) (7 fractions) was crystallised twice from methanol, to give the phenol (XXX or XXXI; R = X = H) (20 mg.) (m. p., mixed m. p., $[\alpha]_D$, and infrared spectrum) characterised as the acetate (m. p., mixed m. p., $[\alpha]_D$, and infrared spectrum). Lumiprednisone acetate (26 mg.) in dioxan (7 ml.) was refluxed for 1 hr., during which no change in rotation occurred. Starting material (m. p., and mixed m. p.) was recovered from the solution.

Androsta-1 : 4-diene-3 : 11 : 17-trione (XXIII).—Prednisone (2·12 g.) in acetic acid (60 ml.) and water (60 ml.) was treated with sodium bismuthate (25 g.) with stirring. After 35 min., 75% of the acetic acid was neutralised by addition of potassium hydroxide (45 g.) in water (300 ml.); the mixture was filtered, the residue was washed with chloroform, and the combined filtrates were extracted with chloroform in the usual way. The crude product, in benzene, was filtered through alumina (Grade V; 15 g.), to give *androsta-1 : 4-diene-3 : 11 : 17-trione* (XXIII) (1·45 g.),

[19] Bellamy, "Infrared Spectra of Complex Molecules," Methuen, London, 1954, p. 64.
[20] Randle and Whiffen, Conference on Molecular Spectroscopy (Institute of Petroleum), Oct. 1954, Paper 12.

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prisms (from benzene–light petroleum), m. p. 196—199°, $[\alpha]_D$ +248° (*c* 1·17), $\lambda_{max.}$ 238 mμ (ε 13,800), $\nu_{max.}$ (Nujol) 1750 (*cyclo*pentanone), 1712 (11-ketone), 1670 (conjugated ketone), and 1630 and 1606 cm.$^{-1}$ (conjugated ethylenic linkages) (Found: C, 76·3; H, 7·65. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·45%). This trione (XXIII) (925 mg.) in dioxan (100 ml.) was irradiated with ultraviolet light under reflux until the rotation had fallen to +141° (19 min.). Chromatography of the product on silica gel (70 g.) and elution with benzene–ether (1 : 2) yielded the *lumi-compound* (XXIV) (20 mg.), prisms (from ethyl acetate–light petroleum), m. p. 179—181°, $[\alpha]_D$ −103° (*c* 0·46), $\lambda_{max.}$ 219, 264 mμ (ε 5500 and 2000 respectively), $\nu_{max.}$ 1746, 1720, 1696, and 1576 cm.$^{-1}$ (Found: C, 76·5; H, 7·75. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·45%).

neo*Prednisone Acetate and Derivatives.*—Prednisone acetate (3 g.) in ethanol (400 ml.) was irradiated in a quartz flask at the b. p. until the rotation had fallen to approx. 0° (about 1 hr.). The products of two such experiments were combined and chromatographed over silica gel (200 g.); after elution with benzene (1·7 l.) to remove the bulk of yellow oily material [chromatography of this fraction over alumina (60 g.) and elution with benzene–chloroform (9 : 1) gave *iso*lumiprednisone acetate (107 mg.), and with benzene–chloroform (6 : 1) gave starting material (1·2 g.)], the column was stripped with acetone and the recovered material rechromatographed over silica gel (200 g.). Six fractions eluted with benzene–chloroform (3 : 2 and 1 : 1) were combined and crystallised, to give neo*prednisone acetate* (XXV) (130 mg.), needles (from methanol), m. p. 230—233°, $[\alpha]_D$ −173° (*c* 0·51), $\lambda_{max.}$ 242 mμ (ε 12,700), in 0·1N-NaOH, $\lambda_{max.}$ 238, 468 mμ (ε 10,700 and 7900 respectively), changing on acidification to $\lambda_{max.}$ 240 and 340 mμ (ε 13,000 and 4200 respectively), $\nu_{max.}$ 1735, 1710, 1658, and 1618 cm.$^{-1}$ (Found: C, 68·85; H, 6·8. $C_{23}H_{28}O_6$ requires C, 69·0; H, 7·05%).

*neo*Prednisone acetate (50 mg.) in methanol (4 ml.) was treated with 0·1N-sodium hydroxide (1·4 ml.), and the red solution immediately acidified with 0·1N-sulphuric acid (2 ml.), after which the mixture was diluted with water (10 ml.) and extracted with ethyl acetate (3 × 20 ml.). The material thus obtained was essentially the enol; to complete the conversion, a solution in methanol (0·5 ml.) was re-treated with alkali and then acid as above, and the material precipitated on dilution with water (4 ml.) collected by centrifugation after good washing with water. The enol formed rosettes (from ethyl acetate–light petroleum), m. p. 228—230°, $\lambda_{max.}$ 242, 340 mμ (ε 11,700 and 3600 respectively), changing in 0·1N-NaOH to 238, 468 mμ (ε 9700 and 7900 respectively), $\nu_{max.}$ (Nujol) 1735 and 1720 (21-acetate and 20-ketone respectively), 1660 (conjugated ketone) and 1605 cm.$^{-1}$ (conjugated ethylenic linkage).

The enol was acetylated in pyridine–acetic anhydride (24 hr.) and worked up in the usual way. Chromatography of the product on alumina (Grade V; 4 g.) and elution with benzene–ethyl acetate (96 : 4) yielded the *enol acetate* (XXVI; R = Ac), needles (from ethyl acetate–light petroleum), m. p. 192—193°, $[\alpha]_D$ +147° (*c* 0·32), $\lambda_{max.}$ 242 and 288 mμ (ε 11,700 and 6800 respectively) changing after 30 min. in 0·1N-NaOH to $\lambda_{max.}$ 238 and 468 mμ (ε 11,600 and 6700 respectively), $\nu_{max.}$ 1749, 1733, 1662, 1621, 1605 cm.$^{-1}$ (Found: C, 67·7; H, 7·0; Ac. 19·45. $C_{25}H_{30}O_7$ requires C, 67·85; H, 6·85; 2Ac, 19·55%).

Ozonolysis of Prednisone Acetate.—Prednisone acetate (200 mg.) in ethyl acetate (20 ml.) was ozonised at −70° for 15 min.; the deep blue solution was kept at −70° until the ultraviolet max. at 240 mμ had disappeared (about 30 min.; in test solutions, the ratio, optical density at 210 mμ : that at 240 mμ, > 4 is desirable). The ozonide was decomposed by evaporation of the solvent under reduced pressure in the presence of water (2 ml.); the residue, in ethyl acetate, was separated through aqueous sodium hydrogen carbonate, to give a neutral fraction (140 mg.) which crystallised readily from ethyl acetate–light petroleum (prisms) to give the *aldehydo-ketone* (XXVII), m. p. 197—199°, $[\alpha]_D$ +105° (*c* 1·12), $\nu_{max.}$ 2725, 1733, and 1701 cm.$^{-1}$ (Found: C, 63·4; H, 7·0. $C_{20}H_{26}O_7$ requires C, 63·5; H, 6·95%).

This work was made possible through the generous financial support of Messrs. Glaxo Laboratories Ltd., who also very kindly supplied the prednisone acetate.

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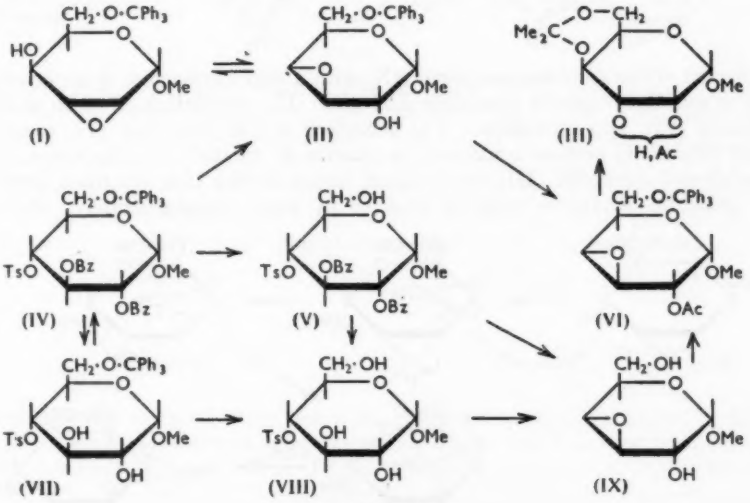
511. *The Behaviour of Derivatives of 3 : 4-Anhydrogalactose towards Acidic Reagents. Part II.*[1]

By J. G. Buchanan.

Methyl 3 : 4-anhydro-α-D-galactoside (IX) has been prepared and converted into the crystalline 2-*O*-acetyl-6-*O*-triphenylmethyl derivative (VI). The latter, with anhydrous hydrogen chloride in acetone, gives methyl *O*-acetyl-4 : 6-*O*-*iso*propylidene-α-D-guloside (III). It is shown that a neighbouring *trans*-*O*-acetyl group exerts a directive influence on the scission of an ethylene oxide by acidic reagents, and carbonium-type intermediates are suggested. The chlorohydrins resulting from the reaction of methyl 3 : 4-anhydro-α-D-galactoside with aqueous hydrochloric acid have been characterised.

Methyl 3 : 4-anhydro-β-D-galactoside was described by Helferich and Müller[2] in 1930. The 6-*O*-triphenylmethyl derivative (II) of the α-anomer was later prepared by Oldham and Robertson,[3] who examined the reaction of its 2-acetate (VI) with acetone containing dry hydrogen chloride. It has recently been shown[1,4] that this preparation of the 3 : 4-epoxide (II) contains an appreciable amount of isomeric 2 : 3-anhydroguloside (I). In order to explain the course of the reactions described by Oldham and Robertson[3] and later by Labaton and Newth[5] it was necessary to prepare the authentic 3 : 4-anhydro-compound in the α-series. This paper describes some of the results obtained.



Oldham and Robertson[3] treated methyl 2 : 3-di-*O*-benzoyl-4-*O*-tosyl-6-*O*-triphenylmethyl-α-D-glucoside (IV) with alkali in hot aqueous acetone to obtain the anhydro-compound (II). Even Labaton and Newth's modified conditions[5] lead to formation of the anhydroguloside (I). The conditions used by Helferich and Müller,[2] a slight excess of sodium methoxide in methanol–chloroform at 0°, were therefore studied. A crystalline

[1] Part I, Buchanan, *J.*, 1958, 995.
[2] Helferich and Müller, *Ber.*, 1930, **63**, 2142.
[3] Oldham and Robertson, *J.*, 1935, 685.
[4] Buchanan, *Chem. and Ind.*, 1954, 1484.
[5] Labaton and Newth, *J.*, 1953, 992.

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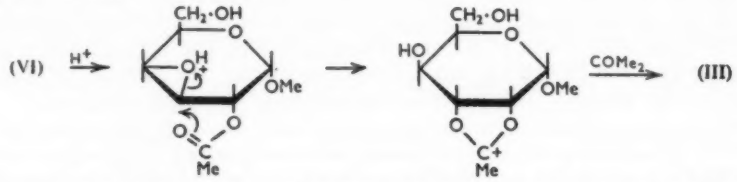
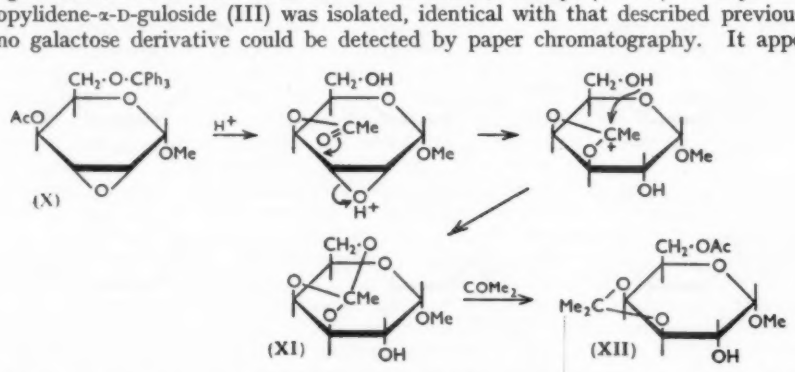
compound was isolated which, however, contained sulphur and was shown to be methyl 4-*O*-tosyl-6-*O*-triphenylmethyl-α-D-glucoside (VII). On benzoylation this gave its dibenzoate (IV) and with alcoholic hydrochloric acid yielded methyl 4-*O*-tosyl-α-D-glucoside (VIII). The structure of the latter was confirmed by periodate oxidation: consumption was very slow, in agreement with the behaviour of certain other 4-substituted glucosides.[1,6]

It therefore seemed unlikely that pure 3 : 4-anhydro-6-*O*-triphenylmethyl-α-D-galactoside (II) could be made by the action of alkali on compound (IV); the use of more drastic conditions would bring about oxide migration. The relative inertness of the toluene-*p*-sulphonyl group was almost certainly due to a conformational effect of the bulky triphenylmethyl group;[7] and this was confirmed by mild treatment of methyl 2 : 3-di-*O*-benzoyl-4-*O*-tosyl-α-D-glucoside[5,8] (V) with alkali, which gave a methyl anhydrohexoside in good yield; the same compound was obtained from the 2 : 3-diol (VIII). The anhydrohexoside was shown to be the 3 : 4-anhydrogalactoside (IX) by hydrolysis with dilute sulphuric acid. As in the β-series,[9] paper chromatography showed that D-gulose and methyl α-D-guloside were the major products, together with methyl α-D-glucoside. No trace of idose or galactose derivatives was present, showing the absence of 2 : 3-anhydroguloside in the anhydro-compound.



Treatment of the anhydro-compound (IX) with a slight deficiency of triphenylmethyl chloride in pyridine[10] gave a crystalline derivative (II), acetylation of which yielded the monoacetate (VI), also crystalline. The behaviour of the pure ester (VI) towards dry hydrogen chloride in acetone could now be examined; methyl (2 or 3)-*O*-acetyl-4 : 6-*O*-*iso*propylidene-α-D-guloside (III) was isolated, identical with that described previously,[1] and no galactose derivative could be detected by paper chromatography. It appears,



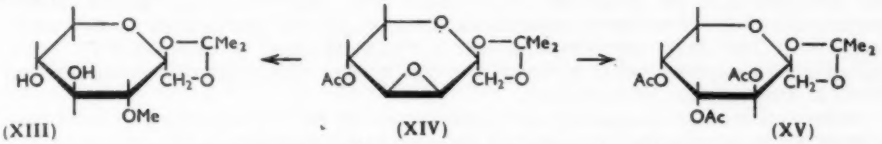
therefore, that the guloside arises from the anhydrogalactoside component of Oldham and Robertson's mixture of anhydro-sugars. In formulating a mechanism for this reaction, three facts must be considered: (*a*) the epoxide ring has suffered *trans*-scission; (*b*) no glucose derivatives were found in the products, in contrast to ring-opening of (IX) by sulphuric or by hydrochloric acid (see below); (*c*) no chlorohydrin was detected in the

[6] Harvey, Michalski, and Todd, *J.*, 1951, 2271; Baddiley, Buchanan, and Szabó, *J.*, 1954, 3826.
[7] Newth, *J.*, 1956, 441.
[8] Bell, *J.*, 1934, 1177.
[9] Müller, *Ber.*, 1935, **68**, 1094.
[10] *Idem*, *Ber.*, 1934, **67**, 421.

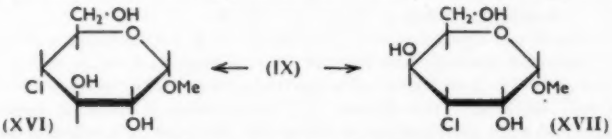
reaction mixture. This implies that the acetyl group exerts a controlling influence on the reaction, and the annexed mechanism (VI) ⟶ (III) is proposed.

Evidence in favour of this mechanism was obtained by hydrolysis of the anhydro-compound (II) and its acetate (VI) by dilute sulphuric acid in aqueous dioxan. Paper chromatography showed that the former gave gulose and methyl α-D-glucoside, but gulose was the only product of hydrolysis of the acetate (VI). Similarly, the anhydro-compound (IX) and its syrupy diacetate were treated with sulphuric acid in aqueous acetone: the former gave methyl α-D-glucoside in addition to gulose derivatives, but no glucose or glucoside was present in the diacetate hydrolysate, methyl tetra-*O*-acetyl-α-D-guloside [11] being isolated in 82% yield after acetylation.

A corollary to the experiments on the pure anhydrogalactoside was that methyl 6-*O*-acetyl-3 : 4-*O*-*iso*propylidene-α-D-galactoside [1] (XII), the other sugar originally isolated from the hydrogen chloride–acetone reaction mixture by Oldham and Robertson,[3] arises from methyl 4-*O*-acetyl-2 : 3-anhydro-6-*O*-triphenylmethyl-α-D-guloside (X). This reaction is of great interest, since none of the idose derivatives, which might be expected to preponderate,[1,12] was detected. The mechanism proposed, (X) ⟶ (XII), through the orthoacetate (XI), has an analogy [13] in the formation of 5-*O*-benzoyl-α-D-ribose 1 : 2 : 3-orthobenzoate by the action of mercuric acetate on 3 : 5-di-*O*-benzoyl-D-ribosyl chloride.



It appears that in the acid-catalysed scission of the oxide rings in both compounds (VI) and (X) the neighbouring *trans*-acetyl group is the major factor deciding the orientation of the product. The only other example in the carbohydrate field is the behaviour of 5-*O*-acetyl-3 : 4-anhydro-1 : 2-*O*-*iso*propylidene-D-tagatose (XIV): [14] with sodium methoxide the product is the D-sorbose derivative (XIII), the first step presumably being deacetylation; acetic anhydride–acetic acid containing a little pyridine gives the D-fructose derivative (XV). The application to other systems is being studied.



It was suggested in Part I [1] that one of the chlorodeoxyhexosides isolated by Labaton and Newth [5] was the 4-chloro-4-deoxyglucoside (XVI); this has now been confirmed. Methyl 3 : 4-anhydro-α-D-galactoside (IX) was treated with aqueous hydrochloric acid in acetone. The two expected chlorohydrins (XVII) and (XVI) were isolated directly by crystallisation from ethyl acetate. The first (45% yield) had m. p. 142°, $[\alpha]_D$ +114·5°, and was clearly different from either of the chlorohydrins isolated earlier.[5] Since it was stable to sodium periodate it was methyl 3-chloro-3-deoxy-α-D-guloside (XVII). The second chlorohydrin (24% yield) was identical with the methyl 4-chloro-4-deoxy-α-D-glucoside (XVI) first made by Labaton and Newth [5] (cf. Part I [1]). When the chlorodeoxyguloside (XVII) was treated with benzaldehyde and zinc chloride a chloroform-soluble *O*-benzylidene compound was formed. This did not crystallise, and its ready solubility in alcohol explains the earlier failure to detect the parent chlorohydrin.[5]

[11] Isbell, *J. Res. Nat. Bur. Stand.*, 1932, **8**, 1.
[12] Reichstein and Sorkin, *Helv. Chim. Acta*, 1945, **28**, 1.
[13] Ness and Fletcher, *J. Org. Chem.*, 1957, **22**, 1465, 1470.
[14] Ohle and Schultz, *Ber.*, 1938, **71**, 2302.

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Experimental

Methyl 2 : 3-Di-O-benzoyl-4-O-tosyl-6-O-triphenylmethyl-α-D-glucoside.—The pure compound was prepared in 79% overall yield from methyl 4 : 6-*O*-benzylidene-α-D-glucoside by Oldham and Robertson's method,[3] with two modifications: (i) Methyl 4 : 6-*O*-benzylidene-α-D-glucoside was benzoylated with excess of benzoyl chloride in pyridine at 100° for 2 hr. The yield of product,[15] m. p. 153°, was 94%. (ii) The triphenylmethyl compound [3,5] was crystallised from chloroform–methanol and then had m. p. 169—170°, $[\alpha]_D^{21}$ +61·8° (*c* 1·66 in $CHCl_3$) (Found: C, 70·9; H, 5·7. Calc. for $C_{47}H_{42}O_{10}S$: C, 70·7; H, 5·3%). The m. p. dropped to *ca.* 160° during storage under normal conditions for several months; the reason was not investigated (cf. Labaton and Newth [5]).

Methyl 2 : 3-Di-O-benzoyl-4-O-tosyl-α-D-glucoside.—The above triphenylmethyl compound (IV) was heated for 1 hr. under reflux in ethanol (300 c.c.) containing concentrated hydrochloric acid (2 drops). The product crystallised in needles; it was filtered off and washed with methanol (yield 12·5 g., 90%), and had m. p. 185°, $[\alpha]_D^{21}$ +99·7° (*c* 1·42 in $CHCl_3$) [5,8] (Found: C, 60·6; H, 4·8; S, 5·8. Calc. for $C_{28}H_{28}O_{10}S$: C, 60·4; H, 5·0; S, 5·8%).

Methyl 4-O-Tosyl-6-O-triphenylmethyl-α-D-glucoside.—The triphenylmethyl compound (IV) (17·0 g.) was dissolved in chloroform (100 c.c.) and treated with sodium methoxide (0·6 g. of sodium) in methanol (100 c.c.) at 0° for 2 hr. Water was added, and the chloroform layer separated, washed with water, and dried (Na_2SO_4). The solution was evaporated to a syrup, and light petroleum (b. p. 40—60°; 1 l.) added. The solid formed was filtered off and recrystallised from chloroform–light petroleum (1 : 3), to give the *ester* as small needles (8·0 g., 64%), m. p. 146—147°, $[\alpha]_D^{20}$ +74·9° (*c* 1·33 in $CHCl_3$) (Found: C, 65·3; H, 6·1; S, 5·1. $C_{33}H_{34}O_9S$·OMe requires C, 67·1; H, 5·8; S, 5·4; OMe, 5·3%). These analytical values were confirmed in 3 independent preparations.

Benzoylation of this compound with excess of benzoyl chloride in pyridine at room temperature for 30 hr. gave the dibenzoate (IV) in good yield (mixed m. p.).

Methyl 4-O-Tosyl-α-D-glucoside.—Methyl 4-*O*-tosyl-6-*O*-triphenylmethyl-α-D-glucoside (4·0 g.), ethanol (50 c.c.), and concentrated hydrochloric acid (0·2 c.c.) were heated under reflux for ½ hr. Chloroform (50 c.c.) was added and the solution evaporated to a syrup. Trituration with ether (50 c.c.) gave the crystalline *toluene*-p-*sulphonate* (2·15 g., 91%), m. p. 147—148° raised by recrystallisation from ethyl acetate–ether to 148—149°, $[\alpha]_D^{22}$ +107·6° (*c* 1·14 in EtOH) (Found: C, 48·3; H, 6·0. $C_{14}H_{20}O_8S$ requires C, 48·3; H, 5·8%). The glycoside (0·11 g.) was treated with sodium metaperiodate (0·19 g.) in water (50 c.c.) at room temperature. Consumption was: 0·23 mol. (16 hr.); 0·40 mol. (43 hr.); 0·65 mol. (112 hr.); 0·89 mol. (211 hr.); 0·98 mol. (282 hr.); 0·98 mol. (331 hr.).

Methyl 3 : 4-Anhydro-α-D-galactoside.—(i) Methyl 2 : 3-di-*O*-benzoyl-4-*O*-tosyl-α-D-glucoside (9·40 g.) in chloroform (50 c.c.) was treated with sodium methoxide (0·5 g. of sodium) in methanol (50 c.c.) at 0° for 5 hr., with occasional shaking. Solid carbon dioxide was added and some solid was removed. The filtrate was evaporated to dryness, dissolved in water (50 c.c.), and extracted with light petroleum (b. p. 40—60°; 50 c.c.) followed by ethyl acetate (20 c.c.). The aqueous layer was evaporated to dryness, and extracted with a boiling mixture (1 : 1) of ethyl acetate and toluene. From the extract the *anhydro-compound* was isolated, by crystallisation from ethyl acetate, as fine needles (2·42 g., 81%), m. p. 118·5—119·5°, $[\alpha]_D^{19}$ +67·5° (*c* 1·11 in H_2O) (Found: C, 48·0; H, 7·1; OMe, 17·9. $C_7H_{12}O_5$ requires C, 47·7; H, 6·9; OMe, 17·6%). Shorter reaction times led to the isolation of some methyl 4-*O*-tosyl-α-D-glucoside, as well as the anhydro-compound (*e.g.*, after 2 hr., 20% of the toluene-*p*-sulphonate and 49% of the anhydro-sugar). The toluene-*p*-sulphonate is sparingly soluble in water and can be extracted from aqueous solution by ethyl acetate. (ii) Methyl 4-*O*-tosyl-α-D-glucoside (1·74 g.), suspended in chloroform (15 c.c.), was treated with sodium methoxide (0·14 g. of sodium) in methanol (15 c.c.) at 0° for 5 hr. The anhydro-compound was isolated as in (i). It crystallised from ethyl acetate–toluene in needles (0·65 g., 74%), m. p. 118—119°, undepressed by the compound prepared as in (i). A sample (*ca.* 5 mg.) was heated with 0·1N-sulphuric acid (0·2 c.c.) at 100° for 1·25 hr. Examination of the product by paper chromatography showed the presence of D-gulose, methyl α-D-guloside, and methyl α-D-glucoside; D-idose,

[15] Ohle and Spencker, *Ber.*, 1928, **61**, 2392; Ansell and Honeyman, *J.*, 1952, 2778; Jeanloz and Jeanloz, *J. Amer. Chem. Soc.*, 1957, **79**, 2579.

D-galactose, and methyl α-D-galactoside were absent (methyl α-D-idoside would have been largely converted into D-idose in these conditions). For R_F values, see Tables.

Methyl 3 : 4-*Anhydro*-6-O-*triphenylmethyl*-α-D-*galactoside*.—The anhydrogalactoside (IX) (2·0 g.) in pyridine (10 c.c.) was treated with triphenylmethyl chloride (2·95 g., 0·93 mol.) for 40 hr. at room temperature. The *glycoside* was isolated by use of chloroform and, crystallised from aqueous methanol, had m. p. 142° (3·77 g., 85%). It recrystallised from ethyl acetate–light petroleum (b. p. 40—60°) as needles, m. p. 144·5°, $[\alpha]_D^{21}$ +8·7° (*c* 3·19 in $CHCl_3$) (Found: C, 74·5; H, 6·6. $C_{26}H_{26}O_5$ requires C, 74·6; H, 6·3%).

The glycoside (*ca.* 5 mg.) was treated with 1 : 1 dioxan–0·2N-sulphuric acid in a sealed tube at 100° for 5 hr. Paper chromatography showed the formation of D-gulose and methyl α-D-glucoside.

Methyl 2-O-*Acetyl*-3 : 4-*anhydro*-6-O-*triphenylmethyl*-α-D-*galactoside*.—The above anhydro-compound (II) (2·0 g.) was acetylated with acetic anhydride in pyridine overnight. Isolated by means of chloroform the *acetate* crystallised from light petroleum (b. p. 60—80°) as plates (2·02 g., 92%), m. p. 119·5—120°, $[\alpha]_D^{21}$ +31·0° (*c* 3·23 in $CHCl_3$) (Found: C, 73·1; H, 6·3. $C_{28}H_{28}O_6$ requires C, 73·0; H, 6·1%). The glycoside (*ca.* 5 mg.) was treated with acid in the same way as the preceding compound. D-Gulose, but no methyl α-D-glucoside, was demonstrated by paper chromatography.

Methyl O-*Acetyl*-4 : 6-O-iso*propylidene*-α-D-*guloside*.—The acetate (VI) (3·78 g.) in acetone (20 c.c.) was treated with acetone (20 c.c.) containing dry hydrogen chloride (1 g.) for 1 hr. at room temperature and the solution then neutralised with anhydrous sodium carbonate. The filtrate after removal of inorganic solid was evaporated to small volume and treated with excess of water containing a little pyridine. The crystalline triphenylmethanol (2·09 g., 98%) was removed and the filtrate extracted several times with chloroform, leaving an aqueous solution, *A*. The combined chloroform extracts were dried (Na_2SO_4) and evaporated to a crystalline mass which was treated with ether and filtered, leaving needles (0·9 g., 40%), m. p. 165—167°, undepressed in admixture with the compound prepared as in Part I.[1] Identity was confirmed by the infrared spectra. The ethereal mother-liquors, which had deposited no further crystalline material,[1,3,5] were evaporated to dryness and deacetylated catalytically.[16] The solution was evaporated, the residue was dissolved in water, and sodium ions were removed in a Dowex 50 (H^+) column. The acidic eluate (pH *ca.* 3) was kept for 48 hr. at room temperature, neutralised with Dowex 3 (OH^-) resin and examined chromatographically. Gulose (a trace) and methyl α-D-guloside were present, together with small amounts of two unidentified spots giving yellow colours with the periodate–Schiff reagent sprays.[17] No galactose or methyl α-D-galactoside was present. The solution *A* above was freed from chloride ions with Dowex 3 (OH^-) resin, concentrated, and subjected to chromatography. A compound with the properties of a methyl mono-*O*-acetyl-α-D-guloside together with a trace of methyl α-D-guloside were the only substances present. Deacetylation gave only methyl α-D-guloside. For R_F values, see Tables.

Methyl 2 : 6-*Di*-O-*acetyl*-3 : 4-*anhydro*-α-D-*galactoside*.—The anhydro-galactoside (IX) (0·5 g.) was treated with acetic anhydride (2 c.c.) in pyridine (5 c.c.) for 24 hr. at room temperature. The diacetate was isolated, by means of chloroform, as a syrup (0·72 g., 97%), $[\alpha]_D^{21}$ +57·4° (*c* 2·86 in $CHCl_3$) (Found: C, 51·2; H, 6·3. $C_{11}H_{14}O_7$ requires C, 50·8; H, 6·2%).

Methyl Tetra-O-*acetyl*-α-D-*guloside*.—The above diacetate (1·49 g.) was heated under reflux with acetone (50 c.c.) and 2N-sulphuric acid (1·5 c.c.) for 4 hr. The solution was neutralised with barium carbonate, filtered, and evaporated to dryness. The residue was deacetylated catalytically [16] and a portion examined by paper chromatography. A heavily loaded chromatogram showed methyl α-D-guloside as the main component, with a small amount of gulose and a minute amount of a fast-running compound (reacting with periodate). Methyl α-D-glucoside could not be detected. The methanol solution was evaporated to dryness and acetylated with acetic anhydride in pyridine. The acetate was isolated in orthodox fashion and crystallised from water, to give prisms (1·70 g., 82%), m. p. *ca.* 95°. Recrystallised from water it had m. p. 98°, $[\alpha]_D^{23}$ +96·5° (*c* 1·16 in $CHCl_3$) (Found: C, 50·0; H, 6·3. Calc. for $C_{15}H_{22}O_{10}$: C, 49·7; H, 6·1%). Isbell [11] gives m. p. 98° and $[\alpha]_D$ +97·3° (in $CHCl_3$).

When methyl 3 : 4-anhydro-D-galactoside was treated with acid under the same conditions, paper chromatography showed the presence of methyl α-D-glucoside in addition to gulose and

[16] Zemplén, Gerecs, and Hadácsy, *Ber.*, 1936, **69**, 1827.

[17] Buchanan, Dekker, and Long, *J.*, 1950, 3162; Baddiley, Buchanan, Handschumacher, and Prescott, *J.*, 1956, 2818.

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methyl α-D-guloside. The glucoside was isolated by crystallisation from ethyl acetate and identified by mixed m. p. and infrared spectrum. For R_F values see Tables.

Paper Chromatography.—The most suitable solvent was butan-1-ol–pyridine–water (3 : 1 : 1 by vol.).[18] Whatman No. 4 paper was used; free sugars were detected by aniline phthalate [19] and glycosides by periodate–Schiff's reagent.[17]

Hexose	R_F	Methyl α-D-hexoside	R_F	Colour * [17]
Galactose	0·21	Galactoside	0·35	GP
Glucose	0·24	Glucoside	0·41	GP
Gulose	0·31	Guloside	0·46	P
Idose	0·41	*O*-Acetylguloside	0·68	P †

* G = Grey, P = purple. † Only after exposure to NH_3.[20]

Methyl 3-Chloro-3-deoxy-α-D-guloside and Methyl 4-Chloro-4-deoxy-α-D-glucoside.—Methyl 3 : 4-anhydro-α-D-galactoside (1·12 g.) in acetone (190 c.c.) containing 2N-hydrochloric acid (5 c.c.) was heated under reflux for 4 hr. The solution was neutralised with lead carbonate, filtered, and evaporated to dryness. The residue was extracted with hot ethyl acetate, and careful crystallisation gave first the pure *guloside* as prisms (0·61 g., 45%), m. p. 142° (decomp.), $[\alpha]_D^{24}$ +114·5° (*c* 1·20 in H_2O) (Found: C, 39·6; H, 6·1; Cl, 16·1. $C_7H_{13}O_5Cl$ requires C, 39·5; H, 6·1; Cl, 16·7%). The glycoside consumed no sodium metaperiodate during 3 days. On nucleation the mother-liquors deposited the glucoside as prisms (0·32 g., 24%), m. p. 114—115°, undepressed in admixture with a specimen prepared by Labaton and Newth's method.[1,5] The identity was confirmed by infrared spectra.

I thank Professor J. Baddiley for his interest and Miss S. Robinson for preparations of methyl 4 : 6-*O*-benzylidene-α-D-glucoside from methyl α-D-glucoside, a generous gift from Messrs. Brown and Polson, Ltd.

KING'S COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE UPON TYNE. [*Received, February 24th,* 1958.]

[18] Hough, Jones, and Wadman, *J.*, 1950, 1702.
[19] Partridge, *Nature*, 1949, **164**, 443.
[20] Baddiley, Buchanan, Hodges, and Prescott, *J.*, 1957, 4769.

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512. *The Synthesis of 2-Phenylisophosphindoline.*

By FREDERICK G. MANN, IAN T. MILLAR, and H. R. WATSON.

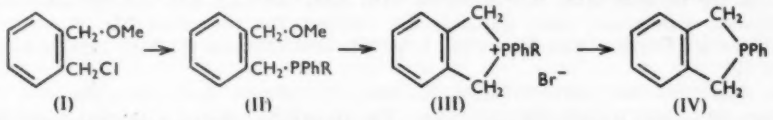
The above phosphine, which has hitherto been very difficult to prepare, has now been synthesised readily and in high yield.
The investigation of two other synthetic routes is briefly recorded.

GREAT interest attaches to 2-phenyl*iso*phosphindoline (IV) because of the nature and variety of its co-ordinated metallic derivatives, but its difficult synthesis has hitherto severely restricted its use. Mann, Millar, and Stewart [1] showed that the interaction of phenylphosphinebis(magnesium bromide), Ph·P(MgBr)$_2$, and *o*-xylylene dibromide gave chiefly an amorphous insoluble powder, which when heated decomposed, producing the crude *iso*phosphindoline in *ca.* 4% yield. Alternatively diphenylphosphine was converted in liquid ammonia into its sodio-derivative, Ph_2PNa, which with *o*-methoxymethylbenzyl chloride (I) gave *o*-methoxymethylbenzyldiphenylphosphine (II; R = Ph); hydrogen bromide converted this phosphine to the *o*-bromomethyl derivative, which rapidly underwent cyclisation by quaternisation to give the bromide (III; R = Ph).

This salt, having two phenyl groups joined to the phosphorus atom, was useless for the preparation of the *iso*phosphindoline (IV) by thermal decomposition. We have now modified this synthesis, in that phenylphosphine in liquid ammonia was treated in turn with 1 equivalent of sodium, ethyl bromide, and again with sodium to promote the sequence, Ph·PH$_2$ ⟶ Ph·PHNa ⟶ Ph·PEtH ⟶ Ph·PEtNa. The last compound

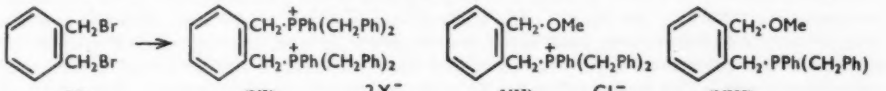
[1] Mann, Millar, and Stewart, *J.*, 1954, 2832.

when treated in the ammonia with the chloride (I) gave ethyl-*o*-methoxymethylbenzylphenylphosphine (II; R = Et) in 72% yield: it was characterised by the preparation of the yellow crystalline dibromobis(phosphine)palladium, $[(C_{17}H_{21}OP)_2PdBr_2]$. A boiling



(I) (II) (III) (IV)

solution of the phosphine (II; R = Et) in acetic acid, when treated with hydrogen bromide, similarly gave 2-ethyl-2-phenyl*iso*phosphindolinium bromide (III; R = Et) in 80% yield. Heating this bromide in nitrogen at 15 mm. gave ethylene, hydrogen bromide, and a distillate consisting of 2-phenyl*iso*phosphindoline (IV) and its hydrobromide, from which the pure phosphine (IV) was isolated in 67% yield.



(V) (VI) (VII) (VIII)

Two syntheses attempted earlier may be briefly recorded. *o*-Xylylene dibromide (V) readily combined with dibenzylphenylphosphine (2 equivalents) to form *o*-xylylenebis-(dibenzylphenylphosphonium) dibromide (VI; X = Br). This salt was also formed when one equivalent of the phosphine was employed, half the dibromide (V) remaining unchanged: this strong tendency for *o*-xylylene dibromide to form the diquaternary salts with tertiary phosphines and arsines, to the apparently complete exclusion of the monoquaternary salts, has been noted before.[1,2] The dibromide (VI; X = Br) was heated in nitrogen at 0·5 mm. in a flask connected to a receiver and a trap cooled in liquid air. After the thermal decomposition was complete, the trap contained hydrogen bromide, benzene, and toluene. The distillate in the receiver gave, on fractionation, 2-phenyl-*iso*phosphindoline (IV) in <10% yield and much dibenzylphenylphosphine and its oxide: the yield of the phosphindoline was variable, and never exceeded this value.

o-Methoxymethylbenzyl chloride combined readily with dibenzylphenylphosphine to give the phosphonium chloride (VII), which on being heated as before afforded benzyl-*o*-methoxymethylbenzylphenylphosphine (VIII). This phosphine with hydrogen bromide in acetic acid gave ultimately a water-insoluble syrup which was not further investigated. The failure of these two routes emphasises further the greater value of the sodium–liquid ammonia method than of the thermal decomposition of phosphonium salts for the preparation of many tertiary phosphines which do not have three identical substituents.[3]

The greater supplies of the *iso*phosphindoline (IV) now available have enabled us to make a detailed investigation (to be reported later) of its co-ordinated derivatives with palladium dihalides in particular, and also with other metallic salts.

Experimental

o-Methoxymethylbenzyl chloride (I) and phenylphosphine were prepared as described by Mann and Stewart,[4] and Mann and Millar [5] respectively.

Ethyl-o-methoxymethylbenzylphenylphosphine (II; R = Et).—A solution of phenylphosphine (31·8 g.) in ether (20 c.c.) was added under nitrogen to liquid ammonia (150 c.c.) in a 3-necked flask equipped with an efficient condenser and a potassium hydroxide guard-tube, and immersed in acetone–carbon dioxide. The vigorously stirred suspension was treated with sodium (6·5 g., 1 equiv.) in small pellets. After 20 min. the intense blue colour was replaced by a deep orange one, and ethyl bromide (31·8 g., 1 mol.) was slowly added. After 30 min. the mixture was treated with sodium (6·4 g.) as before, and finally dropwise with the chloride (I)

[2] Lyon, Mann, and G. H. Cookson, *J.*, 1947, 662.
[3] Hitchcock and Mann, *J.*, 1958, 2081.
[4] Mann and Stewart, *J.*, 1954, 2819.
[5] Mann and Millar, *J.*, 1952, 3039.

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(44·0 g., 0·92 mol.) dissolved in ether (30 c.c.). The solution, on being stirred for 1 hr., became almost colourless. The ammonia was allowed to distil off and the residual sludge treated cautiously with cold boiled water (150 c.c.), followed by ether (50 c.c.). The ethereal layer was separated, the aqueous layer was extracted with ether (30 c.c.), and the combined extracts were washed with water, dried (K_2CO_3), and distilled, the phosphine (II; R = Et) being obtained as a colourless malodorous oil, b. p. 202—206°/13 mm. [51·1 g., 72%, calc. on the chloride (I)].

The oxide and the metho-bromide, -picrate, -perchlorate, and -chloroplatinate of the phosphine all formed uncrystallisable gums. The phosphine reacted with potassium bromopalladite also to form a gum: when, however, air was passed through a solution of this gum in cold light petroleum (b. p. 60—80°), *dibromobis(ethyl-o-methoxymethylbenzylphenylphosphine)-palladium* was deposited, forming yellow crystals, m. p. 129·5—130°, after two recrystallisations from ethanol (Found: C, 50·05; H, 5·1. $C_{34}H_{42}O_2Br_2P_2Pd$ requires C, 50·4; H, 5·2%).

2-Ethyl-2-phenylisophosphindolinium Bromide (III; R = Et).—A vigorous stream of hydrogen bromide was passed through a boiling solution of the phosphine (II; R = Et) (25 g.) in acetic acid (450 c.c.) for 5½ hr. The solvent was removed at 20 mm., and the residual lachrymatory oil shaken with cold boiled water (400 c.c.) and chloroform (250 c.c.) under nitrogen. The chloroform layer was extracted with water (3 × 100 c.c.), but before each extraction it was boiled under reflux for 30 min. to promote quaternisation. The combined aqueous extracts were evaporated at 20 mm., and the residual oily bromide was then dissolved in a minimum of methanol to promote crystallisation, and the solution evaporated to dryness. The colourless residue (23·7 g., 80%), when recrystallised from acetone containing a trace of methanol, afforded the *monohydrated bromide* (III; R = Et), m. p. 273° (decomp., in an evacuated tube): the hydrate was unaffected at 105°/0·5 mm. for 14 hr. (Found: C, 56·0; H, 6·2. $C_{16}H_{18}BrP,H_2O$ requires C, 56·7; H, 5·9%). It gave a yellow *picrate*, m. p. 102—102·5° (from methanol) (Found: C, 56·4; H, 4·4; N, 9·2. $C_{22}H_{20}O_7N_3P$ requires C, 56·3; H, 4·3; N, 9·0%).

2-Phenylisophosphindoline (IV).—The bromide (III; R = Et) (25·0 g.) was placed under nitrogen in a 250 c.c. flask fitted with an air-condenser and a receiver. It was heated at 15 mm. with a brush flame until only a slight carbonaceous residue remained, and a mixture of the phosphine and its hydrobromide had collected in the receiver and the condenser. This product was extracted with a mixture of ether and saturated aqueous sodium carbonate (30 c.c.). The ethereal layer was separated, the aqueous layer extracted with ether, and the combined ethereal extracts, when dried and distilled, gave the phosphine (IV) (11·0 g., 67%), b. p. 182—186°/15 mm., 110—113°/0·2 mm. (lit.,[1] 110—112°/0·2 mm.) (Found: *M*, cryoscopic in benzene, 210. Calc. for $C_{14}H_{13}P$: *M*, 212). It gave a methiodide, m. p. 208—210° (decomp.), after crystallisation from ethanol [lit.,[1] 207—209° (decomp.)].

For experiments requiring small quantities (0·1—0·5 g.) of the phosphine, it was conveniently stored in, and dispensed from, a graduated all-glass syringe of 5 c.c. capacity, fitted with a Polythene cap, and stored under nitrogen.

o-Xylylenebis(dibenzylphenylphosphonium) Dibromide (VI; X = Br).—*o*-Xylylene dibromide (27·7 g.) was added to a solution of dibenzylphenylphosphine [1] (61 g., 2 mol.) in benzene (50 c.c.) under nitrogen. The mixture, which when warmed deposited the syrupy diquaternary salt, was heated under reflux for 30 min., and the solvent decanted: the residual dibromide was washed with benzene and confined in a vacuum over paraffin wax, then forming an almost colourless, hygroscopic, hard glass (88·7 g.), very soluble in the ordinary solvents.

An ethanolic solution, when treated with ethanolic sodium picrate, deposited *o*-xylylenebis(dibenzylphenylphosphonium) dipicrate (VI; X = O·$C_6H_2O_6N_3$), which gave the yellow *monoethanolate*, m. p. 122—124°, on recrystallisation from ethanolic acetone (Found: C, 62·3; H, 4·5; N, 7·2. $C_{60}H_{50}O_{14}N_6P_2,C_2H_6O$ requires C, 62·7; H, 4·75; N, 7·1%).

The dibromide (VI; X = Br) (88 g.) was placed in a flask connected to an air-condenser and receiver, the latter in turn being connected to a trap cooled in liquid air. The salt, under nitrogen at 0·5 mm., when carefully heated with a free flame, fused and then decomposed smoothly at a moderate temperature, giving first a nearly colourless mobile distillate and finally a more viscous amber distillate. A friable black solid residue (4·0 g.) remained.

The trap contained much hydrogen bromide; after removal of this, the colourless liquid residue on fractionation gave benzene (4·6 g.) and toluene (6·7 g.). No benzyl bromide or other product was detected.

The main distillate was shaken under nitrogen with chloroform (50 c.c.) and saturated aqueous sodium carbonate (100 c.c.) for 1 hr., and the organic layer then separated, washed with water, dried (Na_2SO_4), and distilled in nitrogen, giving the fractions: (A) b. p. 116—130°/0·7 mm. (5·8 g.); (B) b. p. 160—210°/0·5 mm. (5·6 g.); (C) b. p. 210—300°/0·5 mm. (20·5 g.).

Fraction (B), which partly solidified, consisted mainly of dibenzylphenylphosphine; it gave dibenzylmethylphenylphosphonium iodide, m. p. and mixed m. p. 204—206° (from ethanol) (lit.,[1] 206—208°) and yellow dibromobis(dibenzylphenylphosphine)palladium crystals (insoluble in ethanol), m. p. and mixed m. p. 236—238° (lit.,[1] 240—242°).

The solid fraction (C) on redistillation gave dibenzylphenylphosphine oxide (from aqueous ethanol), m. p. and mixed m. p. 171° (lit.,[1] 174°).

Fraction (A) on redistillation in nitrogen gave the colourless fractions: (*a*) b. p. 90—100°/0·5 mm. (0·8 g.), a liquid, not identified; (*b*) b. p. 104—108°/0·5 mm. (1·9 g.); and (*c*) b. p. 110—120°/0·5 mm. (1·8 g.). Fraction (*b*) consisted largely of 2-phenyl*iso*phosphindoline; with methyl iodide, it readily gave the crystalline methiodide, m. p. and mixed m. p. 210—211° (Found: C, 50·5; H, 4·5. Calc. for $C_{15}H_{16}IP$: C, 50·85; H, 4·55%). However, it appeared to contain an impurity not readily removable by distillation, since other derivatives were obtained crystalline only with difficulty. Thermal decomposition of the methiodide gives the phosphine only in poor yield,[1] and purification of the ethobromide or ethiodide was difficult; convenient isolation of the pure phosphine by conversion into a quaternary salt and pyrolysis of the latter was thus precluded. Fraction (*c*) also contained the *iso*phosphindoline, identified as above, together with some 2-phenyl*iso*phosphindoline oxide, which separated when set aside and when recrystallised from ethanolic light petroleum (b. p. 40—60°) gave the *monohydrate*, m. p. 98—100° (after drying over P_2O_5 at 60°/0·1 mm.) (Found: C, 68·2; H, 6·2. $C_{14}H_{13}OP,H_2O$ requires C, 68·25; H, 6·2%).

Pyrolysis of an equimolecular mixture of the dibromide (VI; X = Br) with *o*-xylylene dibromide gave only a very small yield of mixed phosphines, together with much unchanged *o*-xylylene dibromide; pyrolysis of mixtures of the salt with smaller proportions of *o*-xylylene dibromide gave results very similar to those noted in detail above.

Dibenzyl-(o-methoxymethylbenzyl)phenylphosphonium Chloride (VII).—*o*-Methoxymethylbenzyl chloride (I) (5·1 g.) in benzene (10 c.c.) was added to dibenzylphenylphosphine (8·5 g., 1 mol.) in benzene (10 c.c.) under nitrogen. No deposition of quaternary salt occurred on boiling the mixture under reflux: the solvent was therefore distilled off, and the residue gently heated for 15 min. before cooling and washing it with light petroleum (b. p. 60—80°). The resulting chloride (VII) formed a hard deliquescent glass, too soluble in all the common solvents for recrystallisation. The corresponding picrate, iodide, nitrate, oxalate, and aurichloride were also too soluble for recrystallisation. The chloride (13·0 g.), when heated under nitrogen at 0·5 mm., fused and decomposed at rather a high temperature, giving first a colourless oily distillate (2·0 g.) and, on stronger heating, a viscous distillate (5 g.). A dark residue, not volatile at a low red heat, remained (3·5 g.).

The viscous distillate was shaken mechanically under nitrogen with chloroform (10 c.c.) and saturated aqueous sodium carbonate (10 c.c.) for 2 hr., and the organic layer then separated, washed with water, dried (Na_2SO_4), and fractionally distilled under nitrogen, giving an oil, b. p. 210—225°/0·5 mm. (0·5 g.), and then benzyl-(*o*-methoxymethylbenzyl)phenylphosphine (VIII), b. p. 275—295°/0·5 mm. (1·4 g., 14%), which crystallised at once in the receiver. No suitable solvent for recrystallisation could be found. A small residue (1 g.) remained.

The phosphine gave a very soluble colourless *methiodide*, m. p. 193—195° (from ethanol–ether) (Found: C, 58·0; H, 5·5. $C_{23}H_{24}OIP$ requires C, 58·0; H, 5·5%), and with aqueous-ethanolic potassium palladobromide it gave orange *dibromobis[benzyl-(o-methoxymethylbenzyl-phenyl)phosphine]palladium*, m. p. 132—133° (from ethanol) (Found: C, 57·0; H, 4·75. $C_{44}H_{46}O_2Br_2P_2Pd$ requires C, 56·5; H, 4·95%).

Passage of dry hydrogen bromide for 3 hr. through a solution of the phosphine in glacial acetic acid at 100°, followed by removal of the solvents and treatment of the residue with chloroform and aqueous sodium hydrogen carbonate, gave a water-insoluble syrup which failed to give a picrate.

We are greatly indebted to Messrs. Albright and Wilson, Ltd., for a grant (to H. R. W.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, February 26th*, 1958.]

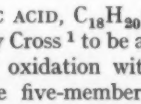
XUM

513. *Gibberellic Acid. Part VII.* The Structure of Gibberic Acid.*

By B. E. Cross, John Frederick Grove, J. MacMillan, and T. P. C. Mulholland.

Gibberic acid is shown to have structure (III), by degradation to the tetramethyl ester (VII; R = Me, R′ = CO_2Me) and to methyl 1 : 7-dimethylfluorene-9-carboxylate (XIV).

Gibberic acid, $C_{18}H_{20}O_3$, an end-product of the acid hydrolysis of gibberellic acid, was shown by Cross [1] to be a benzenoid tetracyclic keto-acid and to possess the partial structure (I) since oxidation with selenium dioxide yielded gibberdionic acid, $C_{18}H_{18}O_4$, a non-enolisable five-membered-ring 1 : 2-diketone. The presence of the hexahydrofluorene nucleus (II) was established by selenium dehydrogenation to 1 : 7-dimethylfluorene [1,2] and by oxidation to benzene-1 : 2 : 3-tricarboxylic acid in significant yield (ref. 3 and see below). Gibberic acid can also be converted [1] into 1 : 7-dimethylfluorene by mild dehydrogenation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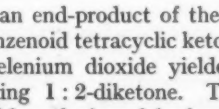
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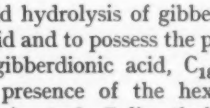
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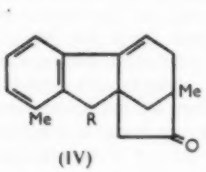
of the tricarboxylic acid, $C_{18}H_{20}O_6$, derived from gibberdionic acid by fission of the 1 : 2-diketone grouping. Skeletal rearrangement is therefore unlikely during the selenium dehydrogenation which thus involves the elimination from gibberic acid of a carboxyl group and of the CH_2·CO group from the feature (I). The position of these groupings in the hexahydrodimethylfluorene nucleus (II) has now been established, leading to structure (III) for gibberic acid, some of the evidence for which has already been briefly reported.[4]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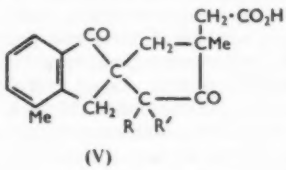
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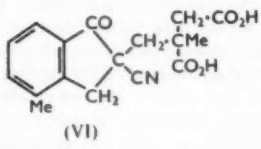
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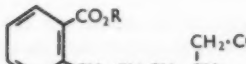
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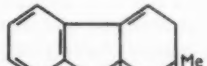
(IX)

The position of the methylenecarbonyl bridge has been determined by the following degradative sequence: (III) ⟶ (IV; R = CO_2H) ⟶ (IV; R = H) ⟶ (V; R = R′ = H) ⟶ (V; RR′ = :N·OH) ⟶ (VI) ⟶ (VII; R = H, R′ = CN) ⟶ (VII; R = H, R′ = CO_2H) ⟶ (VII; R = Me, R′ = CO_2Me).

Oxidation of gibberic acid with alkaline potassium permanganate (4 atom-equiv. of oxygen) at 0° gave a 41% yield of dehydrogibberic acid, $C_{18}H_{18}O_3$ (IV; R = CO_2H), in

* Part VI, *Plant Physiology*, 1958, in the press.

[1] Cross, *J.*, 1954, 4670.
[2] Mulholland and Ward, *J.*, 1954, 4676.
[3] Yabuta, Sumiki, and Aso, *J. Agric. Chem. Soc. Japan*, 1951, **25**, 159.
[4] Cross, Grove, MacMillan, and Mulholland, *Chem. and Ind.*, 1956, 954.

which an ethylenic bond has been introduced in conjugation with the aromatic ring as shown by the ultraviolet spectrum (cf. gibberic acid, Table 1). Dehydrogibberic acid did not undergo either acid or alkaline hydrolysis and regenerated gibberic acid on catalytic reduction. It was rapidly degraded by further alkaline permanganate, a reaction consistent with structure (IV; R = CO_2H); attempts to improve the yield of dehydrogibberic acid by reducing the excess of permanganate led to the recovery of unchanged gibberic acid. The formation of dehydrogibberic acid from gibberic acid presumably involves oxidation of the tertiary hydrogen atom to hydroxyl followed by dehydration.

Oxidation at 25° with more potassium permanganate (10 atom-equiv. of oxygen) gave a low yield of a dibasic acid, $C_{17}H_{18}O_4$, m. p. 255—256° (decomp.), possibly identical with the acid of m. p. 245—247° described by the Japanese workers.[5] Like dehydrogibberic acid the dibasic acid had an ethylenic bond in conjugation with the aromatic ring as shown by the ultraviolet spectrum (Table 1), and took up 1 mol. of hydrogen catalytically. The infrared spectrum showed that the five-membered-ring ketone group of gibberic acid had been lost and the dibasic acid must therefore have the structure (VIII) in which the methylenecarbonyl bridge has been ruptured and the tertiary carboxylic acid group $\beta\gamma$ to the ethylenic bond lost as carbon dioxide.

TABLE 1. *Ultraviolet absorption maxima (mμ) in ethanol.*

Compound	$\lambda_{max.}$	log ε
Gibberic acid	265, 274, 300	2·56, 2·47, 1·49
Dehydrogibberic acid	260, 269, 290, 300	4·14, 4·09, 3·50, 3·44
Acid $C_{17}H_{18}O_4$ (VIII)	265·5	4·01
Gibberone	259·5, 269, 290, 301·5	4·13, 4·07, 3·62, 3·62
Gibberdione	~250, 257, 267, 290, 301	4·14, 4·21, 4·10, 3·65, 3·65
1 : 7-Dimethylfluorene	269, ~275, 293, 297, 304	4·44, 4·37, 3·95, 3·90, 3·95
Methyl 1 : 7-dimethylfluorene-9-carboxylate	~266, 271, ~280, 294, 305·5	4·28, 4·39, 4·25, 3·73, 3·59

Oxidation of gibberic acid at 100° with excess of alkaline permanganate followed by neutral permanganate [6] gave benzene-1 : 2 : 3-tricarboxylic acid (isolated as its methyl ester) in low yield. A low yield (7%) of benzene-1 : 2 : 3-tricarboxylic acid was also obtained by Yabuta *et al.*[3] by means of manganese dioxide in boiling concentrated sulphuric acid. We obtained a better yield (18%) of this acid when the water-soluble gummy by-products from the production of dehydrogibberic acid by alkaline permanganate oxidation of gibberic acid at 0° were re-oxidised with, successively, chromic oxide in acetic acid at 100°, alkaline potassium permanganate at 100°, and neutral permanganate at 20°.

No identifiable product was obtained from the oxidation of gibberic acid with dilute nitric acid, and only acetic acid (isolated as its *p*-bromophenacyl derivative) by oxidation with acid potassium permanganate at 100°. Gibberic acid was largely unaffected by alkaline hydrogen peroxide but a neutral ketone, m. p. 99—101°, was isolated in very low yield.

Decarboxylation of dehydrogibberic acid with palladium–charcoal or charcoal alone at 230° gave the neutral ketone, gibberone (IV; R = H); attempted decarboxylation with copper chromite in 1-methylnaphthalene yielded 0·7 mol. of carbon dioxide but no gibberone. Gibberone can however also be prepared by direct dehydrogenation of gibberic acid. Yabuta *et al.*[7] reported the isolation of gibberone in 17% yield on dehydrogenation of gibberic acid with selenium at 300—330° although they wrongly assigned the molecular formula $C_{18}H_{18}O$ to it. We have confirmed that selenium dehydrogenation of gibberic acid at 360° yields gibberone in low yield, together with 1 : 7-dimethylfluorene: in addition three phenolic substances, A, m. p. 207—210°, B, m. p. 198—202°, and C, m. p. 165—169°, a neutral ketonic substance, m. p. 138—139°, and a highly fluorescent material subliming above 300° were isolated in very small yield.

[5] Yabuta, Sumiki, Aso, Tamura, Igarashi, and Tamari, *J. Agric. Chem. Soc. Japan*, 1941, **17**, 894.
[6] Randall, Benger, and Groocock, *Proc. Roy. Soc.*, 1938, *A*, **165**, 432.
[7] Yabuta, Sumiki, Aso, Tamura, Igarashi, and Tamari, *J. Agric. Chem. Soc. Japan*, 1941, **17**, 975.

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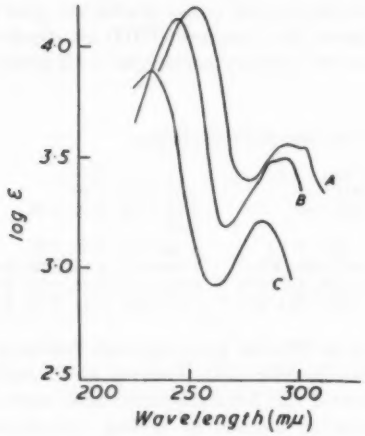
Phenol C is shown in a later paper to be 7-hydroxy-1-methylfluorene; phenol A is a hydroxyfluorene of unknown structure—spectroscopic evidence suggests it may be 2-hydroxy-3 : 8-dimethylfluorene; phenol B is possibly a 2-hydroxyfluorene although the ultraviolet spectrum in alkaline solution does not show the expected bathochromic shift compared with the spectrum in ethanol.

The yield of gibberone by selenium dehydrogenation of gibberic acid on a 50 mg. scale was raised to 27% by plunging the reactants into a bath preheated to 360°; on a larger scale, however, the yield of gibberone decreased and that of 1 : 7-dimethylfluorene increased. Milder methods of dehydrogenation were therefore sought.

Gibberic acid was largely unaffected by iodine in chloroform and by chloranil in tetrachloroethane. The best method of preparing gibberone was found to be by heating gibberic acid with 30% palladium–charcoal. At 340° the yields of 1 : 7-dimethylfluorene



Absorption spectra of (*B*) 2 : 2-*dimethylindan*-1-*one*, (*A*) *the keto-acid* (V; R = R′ = H), *and* (*C*) *the cyano-tricarboxylic acid* (VII; R = H, R′ = CN).

and gibberone were 10% and 49% respectively: at 300° gibberone was the only neutral product isolated, and at 210° the yield of crude gibberone was 70—80%. At the latter temperature only 0·6—0·7 mol. of carbon dioxide was evolved and an acidic product (10—20%), identified as *epi*gibberic acid,[1] was obtained.

These experiments showed that palladium–charcoal at 210—300° was effective in bringing about the decarboxylation of gibberic acid but left the methylenecarbonyl bridge intact. However, the methoxycarbonyl substituent was retained on dehydrogenation of methyl gibberate with 30% palladium–charcoal at 220° and (after hydrolysis) dehydrogibberic acid was obtained.

Gibberone was optically active; in accordance with structure (IV; R = H), the infrared spectrum showed five-membered-ring ketone carbonyl absorption at 1745 cm.$^{-1}$ in CCl_4, and the ultraviolet light absorption (Table 1) showed that the ethylenic bond, revealed by catalytic hydrogenation, was conjugated with the benzene ring. Gibberone was stable to hydrolysis by both acid and alkali. It yielded 1 : 7-dimethylfluorene with selenium at 360° and was oxidised by selenium dioxide in ethanol at 140° to a five-membered-ring 1 : 2-diketone gibberdione (IX), which, like gibberdionic acid,[1] had almost identical ultraviolet absorption spectra in ethanol and in sodium hydroxide; the spectra closely resembled that of gibberone (Table 1).

Gibberone, on oxidation with chromic oxide, yielded a monobasic keto-acid, $C_{17}H_{18}O_4$ (V; R = R′ = H), m. p. 155—157°, which is presumably identical with the uncharacterised acid, m. p. 154—155°, obtained in the same way by Yabuta *et al.*[7] Structure (V; R = R′ = H) is assigned to this acid for the following reasons. The four oxygen atoms

are contained in a carboxyl group and in two carbonyl groupings: one of the carbonyl groups is present in a saturated 5-membered ring (infrared absorption at 1744 cm.$^{-1}$), while the other is conjugated with the aromatic nucleus as shown by the ultraviolet spectrum (Fig. 1) and is contained in an indanone ring system. The formation of the acid (V; R = R′ = H) from gibberone without loss of carbon and with the addition of three oxygen atoms is consistent with the oxidation of a trisubstituted ethylenic double bond to a keto-acid. This acid (V; R = R′ = H) was not hydrolysed by dilute mineral acid or alkali and is not therefore a β-keto acid or β-diketone. Like 2 : 2-dimethylindan-1-one it was stable to neutral permanganate at room temperature and to chromic oxide in acetic acid at 75°: under these conditions both 2-methyl- and 2 : 3-dimethyl-indan-1-one are oxidised.

This evidence suggests that the keto-acid is a 2 : 2-disubstituted indan-1-one, and since it retains the partial structure (I), originally present in gibberic acid, the 5-membered ring must be attached at position 2, as in (V; R = R′ = H).

Oxidation of the keto-acid with alkaline potassium permanganate gave no identifiable products. However, oxidation of 2 : 2-dimethylindan-1-one with potassium permanganate in the presence of magnesium nitrate [8,9] yielded 2 : 2-dimethylindane-1 : 3-dione. Application of this method to the keto-acid gave a complex mixture, resolved by crystallisation and chromatography on paper into benzene-1 : 2 : 3-tricarboxylic acid, 3-methylphthalic acid (isolated as the anhydride), a small amount of β-methyltricarballylic acid, traces of an acid having an R_F value corresponding to oxalic acid, and two unidentified acids (one of them probably formed by further oxidation of β-methyltricarballylic acid which was found to be unstable to oxidation under the conditions employed). The isolation of 3-methylphthalic acid and β-methyltricarballylic acid is consistent with the structure (V; R = R′ = H), final proof of which was obtained by opening both non-benzenoid rings and by an unambiguous synthesis of the product.

Several methods of opening the saturated 5-membered ring in the keto-acid (V; R = R′ = H) were investigated. In contrast to gibberic acid and gibberone, the keto-acid and its ester could not be oxidised to the corresponding 1 : 2-diketones with selenium dioxide. An attempt to prepare hydroxymethylene derivatives of the keto-acid and its ester was likewise unsuccessful. Whilst gibberic acid gave an α-bromo- but no αα-dibromo-derivative, the keto-acid gave an α-bromo-derivative (V; R = H, R′ = Br) in ether and an αα-dibromo-compound (V; R = R′ = Br) with a large excess of bromine in acetic acid, the former giving the latter on further bromination.

The monobromo-derivative (V; R = H, R′ = Br) was resistant to dehydrobromination with collidine, confirming the absence of hydrogen in the α-position to the bromine substituent. Attempted hydrolysis of the bromo-ketones was unsuccessful.

Finally, the keto-acid was treated with butyl nitrite and sodium methoxide [10] to give the desired α-hydroxyimino-compound (V; RR′ = :N·OH) in good yield; Beckmann rearrangement of this with polyphosphoric acid gave the isomeric imide carboxylic acid (X): with toluene-*p*-sulphonyl chloride and sodium hydroxide, however, a tricarboxylic acid (VII; R = H, R′ = CN) was obtained which contained the expected cyano-group (band at 2250 cm.$^{-1}$). Since all six oxygen atoms in compound (VII; R = H, R′ = CN) are present in the three carboxylic acid groups both ketone functions in the acid (V; R = R′ = H) must have been eliminated; and this was confirmed by the infrared spectrum (absence of absorption due to the saturated five-membered ring ketone) and by the ultraviolet spectrum (Fig. 1) which showed the absence of the indanone chromophore and was typical of a substituted benzoic acid. The cyano-tricarboxylic acid, which formed an intramolecular 5-membered-ring anhydride when heated with acetic anhydride, must therefore have structure (VII; R = H, R′ = CN), formed by alkaline hydrolysis of the

[8] Riemschneider, *Gazzetta*, 1947, **77**, 607.
[9] Winkler, *Chem. Ber.*, 1948, **81**, 256.
[10] Koelsch and Le Claire, *J. Org. Chem.*, 1941, **6**, 516.

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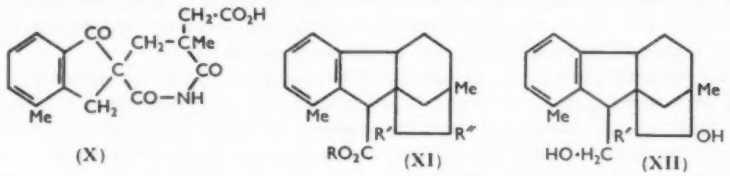
intermediate β-keto-nitrile (VI). The cyano-tricarboxylic acid (VII; R = H, R′ = CN) was not readily oxidised by alkaline potassium permanganate. It was hydrolysed by 50% sulphuric acid to an amorphous tetracarboxylic acid (VII; R = H, R′ = CO_2H) which gave two isomeric tetramethyl esters, m. p. 83—84° and 47—48° (VII; R = Me, R′ = CO_2Me), with diazomethane. These esters, which have different optical rotations, must be diastereoisomers arising from racemisation of the $C_{(2)}$ centre during hydrolysis of the β-keto-nitrile (VI). The structure of the two esters was established by the synthesis [11] of their racemates, m. p. 78—80° and 34—36°, respectively. The infrared spectra of the esters obtained by degradation of gibberic acid and the corresponding synthetic racemates were identical in solution.

The synthesis of the tetramethyl esters (VII; R = Me, R′ = CO_2Me) finally establishes the structure of the keto-acid (V; R = R′ = H) and consequently the structure of gibberone (IV; R = H). It follows that the methylenecarbonyl bridge in gibberic acid must be attached as in (III) and it only remains to prove the position of the carboxyl group.

In an attempt to locate the position of the carboxyl group in gibberic acid by degradation to a substituted 1 : 7-dimethylfluorene wherein the original carboxyl group is retained as a methyl or hydroxymethyl group, the reduction of gibberic acid was studied. Reduction with hydriodic acid and red phosphorus or by the Pondorff method failed: Clemmensen reduction gave deoxogibberic acid (XI; R = R′ = R″ = H). Wolff–Kishner reduction gave a mixture of acids isomeric with deoxogibberic acid, separated by fractional crystallisation into α- and β-isomers. The formation of the two isomers is ascribed to racemisation of more than one of the optically active centres present in gibberic



acid; it was ascertained that on treatment of gibberic acid with sodium ethoxide alone a significant change took place in the optical rotation. Barbier–Wieland degradation of the methyl ester of the α-acid was unsuccessful.

Gibberic acid and methyl gibberate were very resistant to lithium aluminium hydride in ether. Prolonged reduction of gibberic acid with the hydride in boiling tetrahydrofuran gave an amorphous product which was assumed to be the diol (XII; R′ = H). Dehydrogenation of the diol with selenium at 360° not unexpectedly gave 1 : 7-dimethylfluorene with loss of the hydroxymethyl substituent. Reduction of methyl gibberate ethylene ketal by lithium aluminium hydride and regeneration of the 5-membered-ring ketone grouping by hydrolysis furnished an intractable neutral product.

Reduction of methyl gibberdionate with lithium aluminium hydride gave two crystalline products, a *cis*-1 : 2-diol (methyl tetrahydrogibberdionate) (XI; R = Me, R′ = R″ = OH) (C=O at 1735 $cm.^{-1}$), and a triol (XII; R′ = OH), which showed no C=O absorption in the infrared spectrum, gave an inconclusive result with potassium triacetylosmate, and probably contains a *trans*-1 : 2-diol grouping. Attempts to split the triol (XII; R′ = OH) with periodate were unsuccessful but oxidation with sodium bismuthate

[11] Morrison and Mulholland, following paper.

of crude material which contained some of the corresponding *cis*-1 : 2-diol gave an aldehydic gum. Further oxidation of the gum with alkaline silver oxide did not yield the desired alcohol-dicarboxylic acid, but a δ-lactone $C_{18}H_{22}O_3$ of partial structure (XIII).

This approach was abandoned when dehydrogenation of model compounds [12] showed that the conditions necessary for removal of the methylenecarbonyl bridge of gibberic acid by dehydrogenation were sufficiently drastic to eliminate a reduced carboxyl substituent at the 9-position of a fluorene nucleus. Fortunately a convenient method of eliminating the methylenecarbonyl bridge under relatively mild conditions was discovered during an attempt to prepare gibberdione (IX) from gibberdionic acid. With 30% palladium–charcoal at 230° the latter yielded 1 : 7-dimethylfluorene, and treatment of methyl gibberdionate under the same conditions gave the desired methyl 1 : 7-dimethylfluorenecarboxylate and, in low yield, the corresponding ketol $C_{19}H_{22}O_4$. The infrared (C=O at 1736 cm.$^{-1}$ in CCl_4) and ultraviolet spectra (cf. 1 : 7-dimethylfluorene, Table 1) of the 1 : 7-dimethylfluorenecarboxylate indicated that the ester group was unconjugated. The 9-position for the ester substituent was favoured by the fact that alkaline hydrolysis gave a small amount of 1 : 7-dimethylfluorene in addition to the corresponding carboxylic acid.

Structure (XIV) for the ester was confirmed by synthesis. Treatment of the 9-lithium derivative of 1 : 7-dimethylfluorene with solid carbon dioxide [13] afforded 1 : 7-dimethylfluorene-9-carboxylic acid, methylation of which with diazomethane gave the methyl ester identical with the ester obtained by dehydrogenation of methyl gibberdionate.

The isolation of this ester by degradation establishes the position of the carboxyl substituent in gibberic acid which therefore must have structure (III).

Structure (III) for gibberic acid is at variance with the views of the Japanese workers [14] who have advanced the partial structure $C_{16}H_{18}(CO_2H)\cdot COMe$. In support of this structure Seta and Sumiki [15] claimed that the crude product obtained by Beckmann rearrangement of gibberic acid oxime gave a good yield of methylamine on vigorous acid hydrolysis. This experiment has been repeated as the result was inconsistent with the partial structure (I): in our hands a careful examination of the hydrolysis products of the crude mixture from the Beckmann rearrangement (only a portion of which was acidic) failed to reveal the presence of methylamine; about 0·5 mol. of ammonia was produced, estimated as the chloroplatinate. The production of ammonia is not inconsistent with partial structure (I); the remainder of the nitrogen originally present in the oxime was shown to be present, as organic nitrogen, in the other hydrolysis products. An amide-carboxylic acid, isomeric with gibberic acid oxime, $C_{18}H_{21}O_2N$, was isolated from the mixture in low yield.

Experimental

M. p.s are corrected. Microanalyses are by Messrs. W. Brown and A. G. Olney. Light-absorption measurements were obtained as described previously.[2] Unless otherwise stated infrared spectra were determined for " Nujol " mulls and ultraviolet spectra for EtOH solutions.

Gibberic acid [1] was recovered unchanged after 1 hr. in refluxing N-hydrochloric or 2N-sulphuric acid. It did not reduce Tollens's reagent or Fehling's solution and gave no iodoform with iodine and sodium hydroxide.

Bromogibberic Acid.—Gibberic acid (50·4 mg.) was heated under reflux in ether (6·7 ml.) containing bromine (28·9 mg.) until evolution of hydrobromic acid ceased. The residue, after removal of the solvent, was crystallised from ethyl acetate–light petroleum (b. p. 60—80°) and the crystals were separated by hand-picking into needles, m. p. 145—151° (gibberic acid), and aggregates of prisms, m. p. 165—170°. The latter were recrystallised from benzene–light petroleum (b. p. 60—80°), giving *bromogibberic acid*, m. p. 195—196° (Found: C, 59·35; H, 5·35. $C_{18}H_{19}O_5Br$ requires C, 59·5; H, 5·3%). The infrared spectrum showed a carboxylic acid OH band and C=O bands at 1750 (5-membered-ring α-bromo-ketone) and 1709 cm.$^{-1}$ (carboxylic acid).

[12] Cross and Mulholland, unpublished work.
[13] Burtner and Cusic, *J. Amer. Chem. Soc.*, 1943, **65**, 262.
[14] Yatazawa and Sumiki, *J. Agric. Chem. Soc. Japan*, 1952, **25**, 503.
[15] Seta and Sumiki, *ibid.*, 1952, **26**, 508.

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Beckmann Rearrangement of Gibberic Acid Oxime.—Powdered phosphorus pentachloride (0·60 g.) was added in portions during 4 hr. to a stirred solution of the oxime (271 mg.) in dry ether (60 ml.) at 0° ± 1°. After 3·5 hr. at 20°, the mixture was treated with ice, and the ether layer washed with water. The recovered product was heated under reflux with water (5 ml.), giving, on cooling, an amorphous solid (248 mg.), m. p. 80—90° (Found: N, 4·8%). The solid (227 mg., equiv. to 10·9 mg. of N) and 28% hydrochloric acid (4·1 ml.) were heated in a sealed tube at 155—160° for 9 hr. After cooling, the contents of the tube were washed out with water and extracted with methylene chloride. Recovery gave a brown amorphous solid (228 mg.) (Found: N, 2·35% ≡ 5·35 mg. of N).

3N-Sodium hydroxide (20 ml.) was added to the aqueous layer and 16·5 ml. were distilled into concentrated hydrochloric acid (5 ml.) and water (5 ml.). Evaporation yielded a residue (29 mg.) identified as ammonium chloride. No methylamine hydrochloride was detected in the residue by the infrared spectrum. The residue containing ammonium chloride was dissolved in dilute hydrochloric acid, and chloroplatinic acid (150 mg.) in water (1·5 ml.) was added. The ammonium chloroplatinate, determined gravimetrically was equivalent to 6·45 mg. of NH_3 (5·3 mg. of N).

Thus nearly 98% of the nitrogen in the crude Beckmann rearrangement product has been accounted for in the hydrolysis products.

Crystallisation of the brown amorphous solid from ethanol gave an *amide-carboxylic acid* (10 mg.), needles, m. p. 338—343° (decomp.) (Found: C, 71·1; H, 7·2; N, 4·9. $C_{18}H_{21}O_3N$ requires C, 72·2; H, 7·1; N, 4·7%), $\nu_{max.}$ 3260, 3190, ~2600 (broad), 1715, and 1632 cm.$^{-1}$.

Action of Sodium Ethoxide on Gibberic Acid.—Gibberic acid (100 mg.) and ethanol (1·6 ml.) containing sodium (80 mg.) were heated in a sealed tube at 180—190° for 8 hr. The cooled mixture was diluted with water and extracted with ether; the aqueous layer was acidified with concentrated hydrochloric acid and re-extracted with ether giving, on recovery, an intractable gum (78 mg.), $[\alpha]_D^{17}$ −36° (*c* 2·65 in EtOH).

Methyl Gibberate Ethylene Ketal.—Methyl gibberate (108 mg.), ethylene glycol (0·4 ml.), benzene (3 ml.), and toluene-*p*-sulphonic acid (9 mg.) were heated under reflux in a Dean and Stark apparatus for 7 hr. Recovery after washing with aqueous sodium hydrogen carbonate and water furnished a gum (122 mg.) which was chromatographed in light petroleum (b. p. 40—60°) (3 ml.) on alumina (6·5 × 1·3 cm.). Elution with benzene gave a viscous oil (86 mg.) which was distilled at 90°/8 × 10^{-5} mm. giving the oily *ethylene ketal* (Found: C, 73·3; H, 7·8. $C_{21}H_{26}O_4$ requires C, 73·7; H, 7·7%).

Hydrolysis of the ketal (53 mg.) with 90% acetic acid (1 ml.) at 100° for 30 min. and crystallisation of the gummy product from light petroleum (b. p. 60—80°) containing a little benzene gave methyl gibberate, m. p. and mixed m. p. 106—109°.

Reduction of Gibberic Acid.—(1) *Clemmensen method.* Gibberic acid (832 mg.), amalgamated zinc (8 g.), concentrated hydrochloric acid (8 ml.), water (10 ml.), and toluene (10 ml.) were heated under reflux for 72 hr. Portions of concentrated hydrochloric acid (3 ml.) were added after 24 and 48 hr. The toluene was combined with ether extracts of the aqueous layer and washed with dilute hydrochloric acid and water. Recovery gave a gum (830 mg.), separated by Girard's reagent P into a ketonic fraction, which crystallised from ethyl acetate–light petroleum (b. p. 60—80°) in needles of gibberic acid (35 mg.), m. p. 149—152°, and a non-ketonic gum (707 mg.). The gum crystallised from light petroleum (b. p. 40—60°) in prisms of *deoxogibberic acid* (XI; R = R′ = R″ = H) (416 mg.) m. p. 104—108° raised by further crystallisation to 108—110°, $[\alpha]_D^{22}$ +19° (*c* 1·6 in EtOH) (Found: C, 80·15; H, 8·2%; equiv., 268. $C_{18}H_{22}O_3$ requires C, 80·0; H, 8·2%; *M*, 270), $\lambda_{max.}$ ~259, 265, and 273 mμ (log ε 2·48, 2·57, and 2·48 respectively), $\nu_{max.}$ 1706 cm.$^{-1}$ (C=O). Dehydrogenation of deoxogibberic acid with 30% palladised charcoal at 235—240° afforded 0·9 mol. of carbon dioxide but no crystalline product.

(2) *Wolff–Kishner method.* A mixture of gibberic acid (750 mg.), 100% hydrazine hydrate (1·50 ml.), and sodium ethoxide (0·60 g. of sodium in 12 ml. ethanol) was heated in a sealed tube for 8 hr. at 185—190°. The product was diluted with water and extracted with ether; acidification of the aqueous layer with concentrated hydrochloric acid and extraction with ether afforded, on recovery, an oil which partly solidified. The combined product (1·2 g.) from two experiments was separated by fractional crystallisation from light petroleum (b. p. 40—60) and hand-picking of crystals into (*a*), m. p. 118—126°, $[\alpha]_D$ −33° ± 1° (700 mg.), (*b*), m. p. 138—147°, $[\alpha]_D$ −4° ± 2° (239 mg.), and (*c*) mixed residues (150 mg.). Recrystallisation of material

(*a*) from light petroleum gave a *carboxylic acid* (*α-isomer*), laths or prisms, m. p. 124—126°, $[\alpha]_D^{23}$ −33° (*c* 1·22 in EtOH) (Found: C, 80·2; H, 8·1%; equiv., 269. $C_{19}H_{22}O_5$ requires C, 80·0; H, 8·2%; *M*, 270), $\lambda_{max.}$ ~259, 266, 274 mμ (log ε 2·45, 2·54, 2·42 respectively), $\nu_{max.}$ 1698 cm.$^{-1}$ (C=O). Recrystallisation of material (*b*) from light petroleum gave the less soluble *β-isomer*, microcrystalline nodules, m. p. 147—148°, $[\alpha]_D^{18}$ −2° (*c* 1·46 in EtOH) (Found: C, 79·8; H, 8·2%; equiv., 290), $\lambda_{max.}$ ~259, 266, 274 mμ (log ε 2·46, 2·47, 2·46 respectively), $\nu_{max.}$ 1702 cm.$^{-1}$ (C=O). The α-isomer was dimorphic and sometimes melted at 85—95°. Methylation with diazomethane afforded an oily ester which gave a complex mixture of products on treatment with excess of phenylmagnesium bromide in ether–benzene.

(3) *Lithium aluminium hydride.* Here and below, lithium aluminium hydride reductions were worked up either (*a*) with ether as solvent, by decomposition of excess of hydride with 3N-sulphuric acid followed by ether extraction or (*b*) with tetrahydrofuran as solvent, by addition of water, removal of the solvent by steam-distillation and ether-extraction of the acidified aqueous residue.

Gibberic acid (250 mg.) in tetrahydrofuran (20 ml.) was added dropwise to a stirred solution of lithium aluminium hydride (230 mg.) in tetrahydrofuran (25 ml.). The mixture was heated under reflux for 18 hr., lithium aluminium hydride (55 mg.) in tetrahydrofuran (5 ml.) added, and heating continued a further 26 hr. The product, a glass (210 mg.), showed no infrared absorption due to C=O but strong alcoholic hydroxyl absorption.

The glass (185 mg.) and selenium powder (188 mg.) were heated in a current of nitrogen at 340°, rising to 360° during 30 min., and then at 360° for 3·75 hr. The cooled mixture was extracted with ether, and the ethereal extract washed with sodium hydroxide. The recovered gum (145 mg.) in benzene–light petroleum (b. p. 40—60°) (1 : 4; 5 ml.) was chromatographed on alumina (pH 4; 12 g.) in ultraviolet light. Elution of a blue fluorescent band gave a sticky solid (96 mg.) which on sublimation at 60°/10^{-1} mm. and crystallisation from methanol yielded 1 : 7-dimethylfluorene (28 mg.), m. p. and mixed m. p. 104—105°.

Reduction of Methyl Gibberate and its Ethylene Ketal.—These reductions, by lithium aluminium hydride in ether, did not yield useful results.

Reduction of Methyl Gibberdionate.—(*a*) Methyl gibberdionate [1] (102 mg.) in tetrahydrofuran (7 ml.) was added dropwise to lithium aluminium hydride (28 mg.) in tetrahydrofuran (10 ml.) and heated under reflux for 6 hr. The gummy product (100 mg.) was chromatographed in benzene–light petroleum (1 : 1; 1·5 ml.) on alumina (5 × 1·2 cm.) in ultraviolet light. After gummy fractions (total 9 mg.) had been eluted with benzene–light petroleum (2 : 1), benzene–ether (98 : 2), and benzene–ether (95 : 5), elution of a weakly fluorescent band with benzene–methanol (99 : 1) yielded a solid (76 mg.), m. p. 139—146°. Crystallisation from benzene–light petroleum and then aqueous methanol gave *methyl tetrahydrogibberdionate* (XI; R = Me, R′ = R″ = OH), needles m. p. 156—158° (Found: C, 72·2; H, 7·6; OMe, 9·9. $C_{19}H_{24}O_4$ requires C, 72·1; H, 7·65; OMe, 9·9%), $\nu_{max.}$ 3320 cm.$^{-1}$ (OH) and 1735 cm.$^{-1}$ (ester C=O), giving a greenish-yellow colour with potassium triacetylosmate.

(*b*) Methyl gibberdionate (1·30 g.) in tetrahydrofuran (35 ml.) was added to lithium aluminium hydride (0·78 g.) in tetrahydrofuran (70 ml.). After 7 hours' heating under reflux, more lithium aluminium hydride (0·24 g.) was added and heating continued for a further 8 hr. The product, an amorphous solid (1·16 g.), was chromatographed in benzene (10 ml.) on alumina (8 × 2 cm.). The following fractions were collected (eluant in parentheses): (i) 30 mg. of yellow gum (benzene), (ii) 131 mg. of amorphous yellow solid showing a strong infrared C=O band (benzene–methanol, 99 : 1), (iii) 576 mg. of amorphous yellow solid (benzene–methanol 99 : 1), (iv) 272 mg., m. p. 187—195° (benzene–methanol, 95 : 5), and (v) 58 mg., m. p. 226—232° (benzene–methanol 9 : 1).

Fraction (v) crystallised from ethanol–light petroleum (b. p. 60—80°) in prisms, m. p. 234—236°, of a *triol* (XII; R′ = OH) (Found: C, 74·7; H, 8·45. $C_{19}H_{34}O_3$ requires C, 75·0; H, 8·4%). The infrared spectrum showed a strong OH band but no absorption band in the C=O region. The triol gave no colour with potassium triacetylosmate.

Fraction (iv) gave prisms, m. p. 198—200°, which gave an inconclusive result with the osmate reagent. The gum from the crystallisation mother-liquors gave a positive test and contained some *cis*-1 : 2-diol.

Fraction (iii) sublimed at 100—120°/8 × 10^{-5} mm. as an amorphous solid (Found: C, 74·5; H, 8·3%), which consisted of a mixture of stereoisomeric triols showing very weak infrared C=O absorption.

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The triol (XII; R′ = OH) was recovered after 24 hr. at room temperature with excess of sodium metaperiodate in acidified aqueous methanol.

Oxidation of the Triol (XII; R′ = OH).—The triol (122·5 mg.) in 80% acetic acid (9 ml.) was shaken at room temperature for 5·5 hr. with 80% sodium bismuthate (159 mg., 1·1 mol.). Sufficient 3N-sodium hydroxide to neutralise two-thirds of the acetic acid was added with cooling and the solution extracted with benzene. The benzene extract was washed with aqueous sodium hydrogen carbonate and water; the gum [113 mg.; $\nu_{max.}$ 3360 cm.$^{-1}$ (OH), 2759 cm.$^{-1}$ (CH in aldehyde), 1719 cm.$^{-1}$ (C=O)] obtained on recovery was shaken in dioxan (5·25 ml.) for 3·5 hr. with silver oxide [from silver nitrate (300 mg.) in water (0·3 ml.) and 10% sodium hydroxide (2·7 ml.)], and the solution was filtered. After extraction with ether the filtrate was acidified with concentrated hydrochloric acid. Crystallisation of the precipitate from ethanol gave needles, m. p. 180—181°, of a neutral *lactonic alcohol* (XIII) (Found: C, 75·4; H, 7·7. $C_{18}H_{22}O_3$ requires C, 75·5; H, 7·7%), $\nu_{max.}$ 3510 cm.$^{-1}$ (OH) and 1730 cm.$^{-1}$ (lactone C=O), or in CCl_4 3590 and 1734 cm.$^{-1}$.

Oxidation of Gibberic Acid.—(1) *Alkaline potassium permanganate at* 0°. Gibberic acid (254 mg.) in water (2·5 ml.) and saturated aqueous sodium hydrogen carbonate (2·5 ml.) was treated at −1°, during 5 min., with ice-cold 1% potassium permanganate (40 ml.: 4 atoms-equiv. of O) in three portions. After 10 min. at 0°, the mixture was decolorised with sulphur dioxide, acidified with concentrated hydrochloric acid, and set aside for 12 hr. at 0°. The precipitate [105 mg.; m. p. 205—210° (decomp.)] was crystallised from aqueous methanol, then from benzene–light petroleum (b. p. 60—80°), giving *dehydrogibberic acid* (IV; R = CO_2H) (70 mg.), prisms, m. p. 222—224° (decomp.), $[\alpha]_D^{18}$ +99° (*c* 1·0 in EtOH) (Found: C, 76·95; 76·1; H, 6·55, 6·6%; equiv., 276. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%; *M*, 282). In the infrared spectrum it showed a broad band of weak absorption between 3170 and 2600 (carboxylic acid OH) and C=O absorption at 1730 (5-ring ketone) and 1688 (carboxylic acid) cm.$^{-1}$; these bands were found at 1742 and 1711 cm.$^{-1}$ in $CHCl_3$.

The *semicarbazone*, prepared from semicarbazide acetate in ethanol and crystallised from aqueous ethanol, had m. p. 228—230° (decomp.) (Found: C, 66·7; H, 6·25; N, 12·0. $C_{19}H_{21}O_3N_3$ requires C, 67·2; H, 6·2; N, 12·4%).

Dehydrogibberic acid sublimed at 220°/8 × 10^{-4} mm. but evolved carbon dioxide at the m. p. It did not reduce Fehling's solution or Tollens's reagent, gave no iodoform with sodium hypoiodite, and no colour with concentrated nitric acid. Rigorously purified specimens of dehydrogibberic acid gave no colour with concentrated sulphuric acid but preparative-grade specimens derived from gibberic acid by permanganate oxidation gave an intense royal-blue colour. The impurity was removed by methylation (diazomethane), chromatography of the oily methyl ester on alumina, and hydrolysis. Dehydrogibberic acid was recovered after 2 hours' heating under reflux with 5% aqueous potassium hydroxide and with 2N-hydrochloric acid. In sodium hydrogen carbonate solution at 0° it rapidly decolorised potassium permanganate solution.

Dehydrogibberic acid (25·9 mg.) in methanol (3 ml.) took up 0·95 mol. of hydrogen in 42 min. in the presence of 10% palladium–charcoal (17·8 mg.). Crystallisation of the solid product from aqueous ethanol and then from benzene–light petroleum (b. p. 60—80°) gave gibberic acid (16 mg.), m. p. and mixed m. p. 150—152°.

(2) *Alkaline potassium permanganate at* 25°. Aqueous 5% potassium permanganate (17·5 ml.; 10 atom-equiv. of O) was added with stirring during 70 min. to gibberic acid (250 mg.) in 10% aqueous potassium hydroxide (5 ml.) at 25—30°, and the mixture was set aside for 1 hr. The precipitate (37 mg.), obtained on acidification with concentrated hydrochloric acid of the sulphur dioxide-treated solution, crystallised from aqueous ethanol in needles, m. p. 255—256° (decomp.), of an *acid* (VIII) [Found: C, 71·2; H, 6·3%; *M* (Rast), 293; equiv., 142. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%; *M*, 286], $\nu_{max.}$ 3100—2500 and 1700 cm.$^{-1}$ (carboxylic acid). The acid decolorised potassium permanganate in acetone, and microhydrogenation in acetic acid with a palladium catalyst resulted in the uptake (18 min.) of 0·74 mol. of hydrogen. The fluorescein test for a phthalic acid was negative.

(3) *Isolation of methyl benzene-*1 : 2 : 3*-tricarboxylate.* (*a*) Gibberic acid (2·24 g.) was oxidised in 9 equal portions as described in (1) above. After removal of crude dehydrogibberic acid precipitated by acidification, the filtrate was continuously extracted with ether, giving a gum (1·0 g.). The gum in acetic acid (18 ml.) and water (2 ml.) at 100° was oxidised with chromic oxide (3·2 g.) in 90% acetic acid (27 ml.), added portionwise. After 45 min. the solution was

concentrated *in vacuo* to 10 ml. and continuously extracted with ether for 64 hr. The recovered gum (500 mg.) in aqueous 2% potassium hydroxide (50 ml.) was heated under reflux while 3·5% potassium permanganate solution (52 ml.) was added dropwise during 7 hr., and heating was then continued for a further 2 hr. Excess of permanganate was destroyed with methanol, the hot solution was filtered, and the manganese dioxide was washed with hot water. The combined filtrate and washings, adjusted to pH 5 with 3N-hydrochloric acid, were oxidised at 20° with 3·5% potassium permanganate solution (12 ml.). Excess of permanganate was destroyed as described above and the combined filtrate and washings, after acidification with concentrated hydrochloric acid, were continuously extracted with ether for 83 hr. Methylation of the gum (266 mg.) with diazomethane, followed by sublimation at 100—115°/7 × 10^{-2} mm., afforded crude methyl benzene-1 : 2 : 3-tricarboxylate (158 mg., 18%), identified by the infrared spectrum. Repeated crystallisation from ether–light petroleum gave the pure ester, m. p. 95—97° (26 mg.), identical (mixed m. p. and infrared spectrum) with an authentic specimen.

(*b*) Oxidation of gibberic acid (250 mg.) in potassium hydroxide at 100° with excess of potassium permanganate during 7 hr. gave methyl benzene-1 : 2 : 3-tricarboxylate (5 mg.), m. p. 98°.

(4) *Acid potassium permanganate at* 100°. Gibberic acid (96·5 mg.) in N-sulphuric acid (10 ml.) at 100° was treated in portions with solid potassium permanganate (1·16 g.) until no further decolorisation took place and the solution was then distilled. Titration of the aqueous acid distillate with 0·1N-sodium hydroxide showed that 0·73 mol. of volatile acid had been liberated. After evaporation to dryness *in vacuo* the residue in water (0·5 ml.) was adjusted to pH 6, *p*-bromophenacyl bromide (77 mg.) and ethanol (1·2 ml.) were added, and the mixture was heated under reflux for 2 hr. On cooling, *p*-bromophenacyl acetate, m. p. and mixed m. p. 82—84°, separated.

(5) *Alkaline hydrogen peroxide.* Hydrogen peroxide (20-vol.; 10 ml.) was added to gibberic acid (240 mg.) in N-sodium hydroxide (5 ml.), and the whole set aside for 20 days. An additional 5 ml. of hydrogen peroxide were added and the mixture was left for 14 days. Needles, m. p. 99—101°, of a neutral ketone (2 mg.) showing C=O bands at 1746 and 1701 cm.$^{-1}$ were deposited and collected. Acidification of the filtrate gave gibberic acid (184 mg.), m. p. and mixed m. p. 149—152°.

Dehydrogenation of Gibberic Acid.—(1) *Selenium at* 360°. (*a*) The neutral product from the experiment described by Mulholland and Ward [2] was chromatographed on alumina in ultraviolet light and the column eluted with light petroleum (b. p. 40—60°)–ether. After removal of the violet fluorescent band, containing 1 : 7-dimethylfluorene,[2] seven blue fluorescent bands were eluted, all of which gave gummy fractions enumerated below (light petroleum : ether ratio and fraction weight in parentheses):

I (50 : 1; 28 mg.), intractable.

II (20 : 1; 379 mg.). This was rechromatographed on alumina in light petroleum–ether (1 : 1). Solid fractions eluted from a very pale blue band were collected (78 mg., 2%) and repeatedly crystallised from methanol, giving plates or needles (10 mg.) of *gibberone* (IV; R = H), m. p. 126—127°, $[\alpha]_D^{21}$ +27° (*c* 1·76 in acetone) (Found: C, 85·4; H, 7·65. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%), C=O absorption at 1735 cm.$^{-1}$ (1745 cm.$^{-1}$ in CCl_4). The *dinitrophenylhydrazone* crystallised from acetic acid in orange-yellow needles, m. p. 250° (decomp.) (Found: C, 66·1; H, 5·6; N, 12·95. $C_{23}H_{22}O_4N_4$ requires C, 66·0; H, 5·3; N, 13·4%). The *oxime*, prepared from hydroxylamine hydrochloride in pyridine, formed needles (from methanol), m. p. 138—143° (Found: C, 80·2, 81·0; H, 7·6, 7·6. $C_{17}H_{19}ON$ requires C, 80·6; H, 7·6%).

Gibberone sublimed readily at 70°/10^{-4} mm. and gave an intense yellow solution in cold concentrated sulphuric acid. On microhydrogenation in acetic acid with a palladium catalyst it absorbed 0·9 mol. of hydrogen in 7 min. Gibberone was recovered after 5 hours' heating under reflux with 2N-hydrochloric acid and methanol (1 : 1) and after 3 hours' heating under reflux with 3N-sodium hydroxide and methanol (1 : 4).

III (10 : 1; 10 mg.). Rechromatography and elution of the main part of the band with light petroleum–ether (2 : 1) afforded a gum which, after sublimation at 100°/10^{-3} mm. followed by repeated crystallisation from methanol gave prisms, m. p. 138—139°, $\nu_{max.}$ 1730 and 1600 cm.$^{-1}$ in the double-bond stretching region.

IV (5 : 1; 127 mg.), intractable.

V (3 : 1; 52 mg.). Rechromatography and elution of a vivid yellow fluorescent band gave a yellow oil (15 mg.) which solidified under light petroleum (b. p. 60—80°) and thereafter

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crystallised from acetic acid in yellow prisms (3 mg.), subliming at 300—360° without melting. The infrared spectrum showed C=O absorption at 1687 cm.$^{-1}$ and OH absorption at 3350 and 3150 cm.$^{-1}$. Ultraviolet max. were at 272, 282, 305, 312 mμ ($E^{1\%}_{1\,cm.}$ 350, 492, 311, 313, respectively).

VI (2 : 1; 105 mg.). This material sublimed at 115°/10^{-3} mm., giving a solid (23 mg.); chromatography and elution of the column with ether–methanol (99 : 1) then yielded a solid (19 mg.), m. p. 178—180° (decomp.), fractional crystallisation of which from benzene afforded phenols A and B.

Phenol A crystallised in stout needles, m. p. 202—205° (decomp.) (Found: C, 84·55; H, 6·8. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%), $\lambda_{max.}$ ~270, 277, 307, 315 mμ (log ε 4·24, 4·28, 3·93, 3·95 respectively); 301, 316, 327 mμ (log ε, 4·27, 4·21, 4·20 respectively) in 0·1N-sodium hydroxide; the infrared spectrum showed hydroxyl absorption at 3330 cm.$^{-1}$; bands at 781, 856, and 877 cm.$^{-1}$ suggested 1 : 2 : 3- and 1 : 2 : 4 : 5-substitution patterns respectively on the two benzene rings of a fluorene nucleus. The *acetate* formed plates, m. p. 156—157°, from methanol (Found: C, 80·3; H, 6·4. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%). The infrared spectrum showed an absorption band at 1763 cm.$^{-1}$, characteristic of a phenyl acetate, and no hydroxyl absorption. Hydrolysis of the acetate with methanolic sodium hydroxide regenerated phenol A, m. p. 207—210°.

Phenol A was not soluble in cold 2N-sodium hydroxide but dissolved immediately on being warmed and was recovered unchanged. It was not hydrogenated with palladium in acetic acid, and formed a red substance, m. p. 150—155°, with picric acid. It gave a blue-green solution in concentrated sulphuric acid and gave no ferric chloride colour reaction.

Phenol B crystallised from benzene in long needles, m. p. 199—202° (decomp.), depressed to 175—185° on admixture with phenol A; the acetate (C=O at 1755 cm.$^{-1}$) crystallised from methanol in plates, m. p. 167—169° depressed below 145° on admixture with phenol A acetate. Phenol B was soluble in warm 2N-sodium hydroxide from which it was recovered unchanged. It had $\lambda_{max.}$ ~264, 271, ~288, ~305, 313 mμ ($E^{1\%}_{1\,cm.}$ 665, 679, 447, 558, 571 respectively); 245, 252, 277, 328 mμ ($E^{1\%}_{1\,cm.}$ 1104, 1110, 417, 403, respectively) in ethanol–0·1N-sodium hydroxide (2 : 3).

VII (ether; 215 mg.). This fraction, after sublimation at 120°/10^{-3} mm. and repeated crystallisation of the sublimate from benzene–light petroleum (b. p. 60—80°), gave phenol C in long needles (4 mg.), m. p. 165—169°. Recovery of the crystallisation mother-liquors yielded a solid (41 mg.), m. p. 143—160°, which could not be fractionated by chromatography or sublimation, or through the sodium salt. The crude solid (25 mg.), treated in benzene with picric acid (30 mg.), gave red needles, m. p. 128—134° after several crystallisations from benzene. The solid recovered from the purified picrate afforded phenol C, m. p. and mixed m. p. 163—168°.

The benzene mother-liquors from the picrate were chromatographed on alumina (8 × 1 cm.). Elution of a band fluorescing blue with benzene–methanol (99 : 1) and crystallisation of the recovered solid from benzene gave phenol B, large rosettes of needles, m. p. and mixed m. p. 199—210° (decomp.) (acetate, m. p. and mixed m. p. 166—169°). Further elution yielded a solid, m. p. 150—170°.

(*b*) Gibberic acid (45 mg.) and selenium powder (45 mg.) were mixed in a tube (10 × 1·5 cm.) fitted with a side arm 4 cm. from the top, and a slow stream of nitrogen was passed through the apparatus. The tube was plunged into a metal-bath at 360°: there was immediate evolution of carbon dioxide and hydrogen selenide, and a liquid ring condensed on the cool part of the tube. After 2·25 hr. the cooled mixture was extracted with ether and a little gibberic acid removed by extraction with aqueous sodium hydrogen carbonate. The neutral gum (21 mg.) in light petroleum (b. p. 40—60°) was chromatographed on alumina (15 × 1 cm.) in ultraviolet light. Elution of the band fluorescing pale blue gave a solid (17 mg.) from which crude gibberone (10 mg., 27%), m. p. 119—124°, was obtained by sublimation *in vacuo* and crystallisation from methanol.

Repetition of this experiment on a 100 mg. scale gave a reduced yield of gibberone and some 1 : 7-dimethylfluorene.

(2) *Palladium–charcoal.* (*a*) At 340°. Gibberic acid (104 mg.) and 30% palladium–charcoal (52 mg.; Zelinsky and Turowa-Pollak [16]) were heated in a current of nitrogen from 165° to 320° in 50 min. and then kept at 320—340° for 110 min. The cooled mixture was extracted with ether, and the extract washed with aqueous sodium hydrogen carbonate. The neutral fraction

[16] Zelinsky and Turowa-Pollak, *Ber.*, 1925, **58**, 1295.

(68 mg.) in light petroleum (b. p. 60—80°) (4 ml.) was chromatographed on alumina (5 × 1 cm.) in ultraviolet light. Elution of a weakly fluorescent band with light petroleum–ether (99 : 1) gave 1 : 7-dimethylfluorene (7·5 mg.) (from methanol), m. p. and mixed m. p. 104—106°. Further elution of a blue fluorescent band with light petroleum–ether (9 : 1) gave a solid (4·3 mg., 49%), m. p. 85—107°. Crystallisation from methanol afforded gibberone, m. p. and mixed m. p. 116—122°.

At 300° (6 hr.) gibberic acid (105 mg.) with 30% palladium–charcoal evolved carbon dioxide (1 mol.) and gave gibberone (35 mg.), m. p. 120—122°.

(*b*) At 210°. Gibberic acid (140 mg.) and the above catalyst (90 mg.) were heated in the apparatus described above for 80 min. at 210°. 0·73 Mol. of carbon dioxide was evolved. The neutral fraction (84 mg., 72%) consisted of crude gibberone. The acid fraction (27 mg.) recovered from the sodium hydrogen carbonate washings crystallised from methanol in needles, m. p. 250—253°, of *epi*gibberic acid [1] (Found: C, 75·8; H, 7·1. Calc. for $C_{18}H_{20}O_5$: C, 76·0; H, 7·1%).

The yields from ten similar experiments fell in the range: carbon dioxide, 0·6—0·85 mol.; *epi*gibberic acid, 10—20%; crude gibberone 80—70%. Pure gibberone (1·34 g.) was obtained from the crude gibberone (4·59 g.) by chromatography on alumina followed by repeated crystallisation from methanol. Crude gibberone was used directly in the oxidation with chromic oxide described below.

Decarboxylation of Dehydrogibberic Acid.—(a) *Palladium–charcoal.* A mixture of dehydrogibberic acid (56·2 mg.) and 30% palladium–charcoal (30 mg.) was heated in a slow stream of nitrogen at 190°, rising to 230° during 30 min., and then at 230—240° for 1·5 hr. (1·0 mol. of carbon dioxide evolved). The charcoal was extracted with ether, and the extract washed with aqueous sodium hydrogen carbonate. Recovery furnished a yellow solid (42 mg.) which was chromatographed in light petroleum (b. p. 60—80°)–ether (20 : 1) on alumina (2·5 × 1·0 cm.) in ultraviolet light. A semi-solid forerun (7 mg.) was rejected: elution of a blue fluorescent band gave a solid (33 mg.) which crystallised from methanol in plates of gibberone, m. p. and mixed m. p. 125—127°.

(b) *Charcoal.* The experiment was carried out as in (a), except that charcoal (30 mg.) was used and the temperature was raised from 190° to 230° during 10 min. 0·94 Mol. of carbon dioxide was evolved. Chromatography of the neutral fraction gave crude gibberone (25 mg.).

(c) *Copper chromite.* Dehydrogibberic acid (56·4 mg.) and copper chromite (58 mg.) in 1-methylnaphthalene (1·0 ml.) were heated in a current of nitrogen under reflux for 1·5 hr. 0·70 Mol. of carbon dioxide was evolved but the product was intractable.

Fusion of dehydrogibberic acid at 235° in the presence of copper chromite yielded carbon dioxide (0·58 mol.), some unchanged dehydrogibberic acid, and an intractable neutral gum.

Dehydrogenations with 30% *Palladium–Charcoal.*—(1) *Methyl gibberate.* The ester (266 mg.) and the catalyst (100 mg.) were heated at 220—230° for 1·5 hr. in a slow stream of nitrogen. The filtered ether extract of the reaction mixture was washed with aqueous sodium hydrogen carbonate and water, and the recovered neutral gum (264 mg.) was chromatographed in light petroleum (b. p. 40—60°) on alumina (14 × 1 cm.). Fractional elution (25 ml. portions) with ether–light petroleum (1 : 4) afforded a gum (152 mg.) which was hydrolysed by heating it in methanol (5 ml.) and 20% aqueous potassium hydroxide (0·8 ml.) for 2 hr. Removal of the methanol *in vacuo*, acidification of the residue, and crystallisation of the crude acidic product from methanol yielded prisms (76 mg.), m. p. and mixed m. p. with dehydrogibberic acid 217—220° (decomp.).

(2) *Gibberdionic acid.* The acid (85 mg.) and the catalyst (29 mg.) were heated as described in (1) above. The recovered neutral gum (33 mg.) crystallised from methanol in needles (20 mg.), m. p. and mixed m. p. with 1 : 7-dimethylfluorene 104—106°. The acidic fraction (22 mg.) was intractable.

(3) *Methyl gibberdionate.* The ester (250 mg.) and the catalyst (100 mg.) were heated as described in (1). The recovered neutral yellow gum (196 mg.) was triturated with ether (10 ml.), and insoluble starting material filtered off (5 mg.). The ether solution was passed through a column of alumina (13 × 1 cm.) in ultraviolet light. After elution of a pale blue fluorescent band which furnished a yellow gum (*A*) (105 mg.) on recovery, elution with benzene of a band, pale yellow in daylight, furnished a yellow gum (*B*) (31 mg.).

Crystallisation of *B* from methanol gave needles, m. p. 195—205° (22 mg.), which on further crystallisation from ethyl acetate afforded hexagonal plates (10 mg.) of a *ketol*, m. p. 208—215°

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(Found: C, 72·6; H, 7·05. $C_{19}H_{22}O_4$ requires C, 72·6; H, 7·05%), $\lambda_{max.}$ ~260, 266, 273·5 mμ (log ε 2·53, 2·62, 2·58 respectively), $\nu_{max.}$ 3140 (OH) and 1740 cm.$^{-1}$ (C=O) (1745 cm.$^{-1}$ in $CHCl_3$; intensity equivalent to two C=O groups).

Crystallisation of *A* from methanol gave *methyl* 1 : 7-*dimethylfluorene*-9-*carboxylate* (XIV) (52 mg.), needles, m. p. 121—122°, $[\alpha]_D^{21}$ −5° ± 3°, $[\alpha]_{5461}^{21}$ −0·5° ± 3° (*c* 1·92 in EtOH) (Found: C, 80·7; H, 6·6; OMe, 12·9. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4; OMe, 12·3%), $\nu_{max.}$ 1731 cm.$^{-1}$ (C=O) (1736 cm.$^{-1}$ in CCl_4). This ester was identical (mixed m. p. and infrared spectrum) with a synthetic specimen (see below).

Hydrolysis of the ester (33 mg.) in hot methanol (2 ml.) and 40% aqueous potassium hydroxide (2 ml.) for 3 hr. gave 1 : 7-dimethylfluorene (3 mg.), m. p. 102—105° (identified by mixed m. p. and infrared spectrum), and 1 : 7-*dimethylfluorene*-9-*carboxylic acid* (30 mg.), which crystallised from acetic acid in needles, m. p. 221—223° (decomp.), $[\alpha]_D^{18}$ +3° ± 3°, $[\alpha]_{5461}^{18}$ +1° ± 3° (*c* 1·32 in 0·1N-NaOH) (Found: C, 80·0, 80·0; H, 6·1, 5·95%; equiv., 238. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%; *M*, 238), $\lambda_{max.}$ ~260, 271, ~280, 306 mμ (log ε 4·19, 4·33, 4·18, 3·65, 3·60 respectively), $\nu_{max.}$ 1691 (C=O) and 3100—2500 cm.$^{-1}$ (OH) (identical with the synthetic specimen described below).

1 : 7-*Dimethylfluorene*-9-*carboxylic Acid*.—Lithium (0·32 g.) in ether (12 ml.) was treated with a few drops of a solution of butyryl chloride (1·84 g.) in ether (6·0 ml.). When the reaction started, the mixture was cooled to −40° during the addition (30 min.) of the rest of the reagent. The temperature of the stirred solution was allowed to rise to 20° during 4 hr. and, after the addition of 1 : 7-dimethylfluorene (2·90 g.) in portions, the mixture was heated under reflux for 1 hr., diluted with ether (8 ml.), cooled to −40°, and poured on freshly crushed solid carbon dioxide. When the temperature of the mixture reached 20°, water was added and the aqueous layer was separated, washed with ether, and acidified with concentrated hydrochloric acid. The precipitate (2·85 g.), m. p. 214—217° (decomp.), crystallised from acetic acid in needles m. p. 221—222° (decomp.), of 1 : 7-dimethylfluorene-9-carboxylic acid (Found: C, 80·0; H, 6·0%), identical (infrared spectrum) with the acid obtained above by dehydrogenation of methyl gibberdionate.

The methyl ester (XIV) crystallised from methanol in needles, m. p. 119—120° (Found: C, 81·0; H, 6·3%). It was identical (mixed m. p. and infrared spectrum) with the ester derived from methyl gibberdionate.

The *ethyl ester* crystallised from light petroleum (b. p. 40—60°) in prisms, m. p. 69—70° (Found: C, 80·95; H, 7·0. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%).

Dehydrogenation of Gibberone.—Gibberone (45 mg.) and selenium powder (45 mg.) were heated at 360° in a stream of nitrogen in the apparatus described above for the selenium dehydrogenation of gibberic acid. Carbon dioxide was evolved but no volatile carbonyl compounds (2 : 4-dinitrophenylhydrazine trap) were detected. After 1 hr. the cooled mixture was extracted with ether, and the ether extracted with aqueous sodium hydrogen carbonate (no acidic material recovered). The recovered neutral gum (27 mg.) in light petroleum (b. p. 40—60°) was chromatographed on alumina (15 × 1 cm.) in ultraviolet light. Elution of a band fluorescing violet gave 1 : 7-dimethylfluorene (5 mg.), m. p. and mixed m. p. 105—107°. A band fluorescing pale blue, eluted with light petroleum–ether (50 : 1), gave gibberone (11 mg.).

Oxidation of Gibberone.—(1) *Chromic oxide*. To gibberone (47 mg.) in acetic acid (1·0 ml.) was added portionwise chromic oxide (80 mg., 6 atom-equiv. of O) in acetic acid (0·5 ml.) and water (0·2 ml.). After each addition the mixture was heated at 100° until the oxidant was consumed and the process continued until excess of chromic oxide was present (1 hr.). After the addition of water (10 ml.) continuous extraction with benzene afforded a gum which was extracted with aqueous sodium hydrogen carbonate. The acid fraction, recovered in ethyl acetate, solidified when rubbed with ether and crystallised from benzene–light petroleum (b. p. 60—80°) in needles (20 mg., 35%), m. p. 155—156°, $[\alpha]_D^{18}$ +27° (*c* 0·93 in acetone), of 4-*methyl*-1-*oxoindane*-2-spiro-1′-(4′-*methyl*-3′-*oxocyclopentane*-4′-*acetic acid*) (V; R = R′ = H) (Found: C, 71·5; H, 6·5%; equiv., 268. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%; *M*, 286), $\lambda_{max.}$ ~248, 254, 293, ~302 mμ (log ε 4·16, 4·18, 3·55, 3·54 respectively), $\lambda_{max.}$ (in 0·1N-NaOH) ~250, 256, 288, 298, ~305 mμ (log ε 4·08, 4·13, 3·34, 3·42, 3·38 respectively). The infrared spectrum showed broad OH absorption at 3130 cm.$^{-1}$ and C=O bands at 1740 and 1713 cm.$^{-1}$: in dioxan it showed C=O bands at 1744 (5-membered-ring ketone), 1738 (monomeric carboxylic acid), and 1715 cm.$^{-1}$ (indanone-carbonyl).

The *methyl ester*, prepared with diazomethane, crystallised from benzene–light petroleum (b. p. 40—60°) in needles, m. p. 129—130° (Found: C, 71·9; H, 6·75; OMe, 11·0. $C_{18}H_{20}O_4$ requires C, 72·0; H, 6·7; OMe, 10·3%), $\lambda_{max.}$ ~249, 254, ~295, 300 mμ (log ε 4·14, 4·16, 3·49, 3·50 respectively), $\nu_{max.}$ (C=O) 1735 and 1702 cm.$^{-1}$ (1744 and 1717 cm.$^{-1}$ in CCl_4).

The keto-acid (V; R = R′ = H) gave a precipitate with dinitrophenylhydrazine in 2N-hydrochloric acid. It gave colourless solutions in concentrated sulphuric acid or ferric chloride. It was recovered unchanged after 4 hours' heating with 2N-hydrochloric acid and after 3 hours' heating with 3N-sodium hydroxide. Both the acid and its methyl ester were saturated to potassium permanganate in acetone and were not oxidised by chromic oxide in aqueous acetic acid at 70—80°. Neither the acid nor its methyl ester gave crystalline hydroxymethylene derivatives with ethyl formate and sodium methoxide.

When the oxidation was repeated with crude gibberone the yield of pure keto-acid was 23%.

(2) *Selenium dioxide.* Gibberone (80 mg.) in ethanol (0·3 ml.) was heated with selenium dioxide (44 mg.) in a sealed tube at 140° for 4 hr. Filtration of the cooled mixture and recovery gave an orange gum (90 mg.) which was chromatographed in ether (50 ml.) on alumina (pH 4; 12 × 1 cm.) in ultraviolet light. Elution with ether gave (*a*) a yellow gum (30 mg.) from a greenish-yellow fluorescent band (several crystallisations from methanol afforded gibberone), (*b*) a yellow gum (8 mg.) from an interband, and (*c*) an orange gum (33 mg.) from a dull greenish-brown band. Several crystallisations of (*c*) from benzene–light petroleum (b. p. 60—80°) gave orange-yellow needles (12 mg.) of *gibberdione* (IX), m. p. 181—182° (Found: C, 80·3; H, 6·4. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%), $\lambda_{max.}$ in EtOH–0·1N-sodium hydroxide, 250, 257·5; 267, 290, 301 (log ε 4·12, 4·18, 4·07, 3·66, 3·62 respectively), $\nu_{max.}$ (C=O) 1745 cm.$^{-1}$, shoulder at 1757 cm.$^{-1}$.

The yield of gibberdione was lower when heating was continued for 8 hr. No oxidation of gibberone took place with selenium dioxide at 110° in ethanol in a sealed tube; in boiling acetic acid only gums were obtained.

Bromination of the Keto-acid (V; R = R′ = H).—(a) *In ether.* A solution of bromine (170 mg., 5 mol.) in ether (10 ml.) was added to a suspension of the keto-acid (57 mg.) in ether (4 ml.) until the yellow colour persisted for 15 min. After 12 hr. the solution was washed with water and the solute recovered. The gummy product solidified on trituration with benzene and crystallised from ethyl acetate–light petroleum (b. p. 60—80°) in rods (16 mg.) of the 2′-*bromo-ketone* (V; R = H, R′ = Br), m. p. 178—182° or 199—203° (Found: C, 56·0; H, 4·7; Br, 21·7. $C_{17}H_{17}O_4Br$ requires C, 55·9; H, 4·7; Br, 21·9%). The two forms were interconvertible by seeding with the appropriate crystalline modification, and had $\lambda_{max.}$ ~250, 256, 292, 300 mμ (log ε 4·03, 4·06, 3·30, 3·32 respectively). Infrared spectra: high-m. p. form, C=O bands at 1756, 1749, ~1729, 1722, and 1708 cm.$^{-1}$: low-m. p. form, C=O bands at 1748 1728, 1705 cm.$^{-1}$. In dioxan both forms had identical spectra (C=O bands at 1766, 1734, and 1719 cm.$^{-1}$). The bromo-ketone was recovered after being heated under reflux for 4 hr. with collidine.

(b) *In acetic acid.* Bromine (128 mg., 8 mol.) was added to the keto-acid (29 mg.) in acetic acid (2 ml.) containing 48% hydrobromic acid (0·03 ml.), and the solution was set aside in the dark for 8 days. The solid obtained by evaporation of the solvent *in vacuo* crystallised from benzene–light petroleum (b. p. 60—80°) in needles (26 mg.), m. p. 205—207° (decomp.), of the 2′ : 2′-*dibromo-ketone* (V; R = R′ = Br) (Found: C, 45·5; H, 3·75; Br, 36·2. $C_{17}H_{16}O_4Br_2$ requires C, 46·0; H, 3·6; Br, 36·0%), $\nu_{max.}$ (C=O) 1764 and 1707 cm.$^{-1}$.

Bromination of the monobromo-ketone (48 mg.) in acetic acid at room temperature in the dark during 14 days afforded the dibromo-ketone (44 mg.), m. p. and mixed m. p. 203—205°.

The dibromo-ketone (41 mg.) in collidine (0·5 ml.) was heated under reflux for 1 hr. After removal of collidine hydrobromide (22 mg.) acidification of the filtrate with 3N-hydrochloric acid gave a dark-red oil which slowly solidified. Recovery of a filtered ether solution gave the monobromo-ketone (8 mg.), m. p. and mixed m. p. 199—203°.

Nitrosation of the Keto-acid (V; R = R′ = H).—The keto-acid (120 mg.) in methanol (0·5 ml.) was treated with sodium (30 mg.) in methanol (0·5 ml.), followed by butyl nitrite (0·1 ml.). After 6 days the yellow solution was diluted with water (0·5 ml.). Acidification with 3N-hydrochloric acid afforded needles (130 mg.), m. p. 224—226° (decomp.), which after being washed with benzene followed by recrystallisation from acetic acid gave prisms, m. p. 238—240° (decomp.), of the 2′-*hydroxyimino-derivative* (V; RR′ = :N·OH) (116 mg.) (Found: C, 64·7; H, 5·5; N, 4·6. $C_{17}H_{17}O_5N$ requires C, 64·75; H, 5·4; N, 4·4%), $\lambda_{max.}$ 228, 234, 277·5 mμ (log ε

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4·01, 3·99, 4·43 respectively), $\lambda_{max.}$ (in 0·1N-NaOH) ~280, 320 mμ (log ε 4·01, 4·34 respectively), $\nu_{max.}$, OH at 3260 cm.$^{-1}$ and double-bond stretching region at 1746, 1730, 1677, 1610, and 1595 cm.$^{-1}$ (in dioxan 1724 and 1625 cm.$^{-1}$).

Beckmann Rearrangement of the 2′-Hydroxyimino-keto-acid (V; RR′ = :N·OH).—(a) *With toluene-p-sulphonyl chloride.* The above 2′-hydroxyimino-derivative (265 mg.) of the keto-acid, toluene-*p*-sulphonyl chloride (270 mg.), and 10% aqueous sodium hydroxide (1·0 ml.) were heated at 110—130° for 15 min. with vigorous stirring. Acidification of the cooled mixture gave a solid which was washed with benzene, followed by ether. The product (221 mg.; m. p. 180—182°) crystallised from 20% aqueous methanol in needles, m. p. 188—189° (decomp.), of 3-*carboxy*-6-(2-*carboxy*-6-*methylphenyl*)-5-*cyano*-3-*methylhexanoic acid* (VII; R = H, R′ = CN) [Found: C, 61·4; H, 5·8; N, 4·6%; equiv., 113. $C_{17}H_{19}O_6N$ requires C, 61·25; H, 5·75; N, 4·2%; equiv. (tribasic), 111], $\lambda_{max.}$ 233, 284, ~293 mμ (log ε 3·89, 3·21, 3·08 respectively), $\nu_{max.}$ ~1660 (shoulder), 1696 (broad), 2250 and ~2400 — ~3150 cm.$^{-1}$ (broad) [in dioxan ~1730 — 1721 cm.$^{-1}$ (broad)].

The nitrile gave no colour with ferric chloride or with concentrated sulphuric acid; it did not give a precipitate with Brady's reagent and was only very slowly oxidised by alkaline potassium permanganate at room temperature.

The nitrile, heated under reflux for 1 hr. with acetic anhydride, gave a glassy anhydride which regenerated the nitrile in hot water. The anhydride after sublimation at 10^{-3} mm. showed infrared bands at 3100—2500 (broad, carboxylic acid OH), 2240 (C≡N), 1860 and 1775 (5-membered-ring anhydride), and 1700—1630 cm.$^{-1}$ (broad, carboxylic acid C=O).

(b) *With polyphosphoric acid.* The hydroxyimino-compound (180 mg.) and polyphosphoric acid (6·5 g.) were stirred at 130° for 15 min. After cooling and dilution with water the resulting precipitate was filtered off and extracted with cold sodium hydrogen carbonate solution. Acidification of the extract with hydrochloric acid and filtration gave an *imide-carboxylic acid* (X) (105 mg.), m. p. 242—243° (decomp.), which crystallised from acetic acid in prisms, m. p. 243—245° (decomp.) (Found: C, 64·4; H, 5·7; N ,4·4%; equiv., 328. $C_{17}H_{17}O_5N$ requires C, 64·75; H, 5·4; N, 4·4%; *M*, 315), $\nu_{max.}$ 3360, ~3140, 1739, 1722, 1691, 1593 cm.$^{-1}$.

Hydrolysis of the Nitrile (VII; R = H, R′ = CN).—Hydrolysis of the nitrile (260 mg.) with boiling 50% sulphuric acid (4·0 ml.) in nitrogen for 7·5 hr. gave a clear solution. Only a trace of carbon dioxide was evolved. On cooling, an oil separated which appeared to solidify. Ether-extraction of the mixture and recovery gave a gum, which on trituration with light petroleum gave an amorphous solid, α + β-3 : 5-*dicarboxy*-6-(2-*carboxy*-6-*methylphenyl*)-3-*methylhexanoic acid* (VII; R = H, R′ = CO_2H) (268 mg.), m. p. 175—179° [Found: C, 58·1; H, 5·8%; equiv., 90. $C_{17}H_{20}O_8$ requires C, 57·95; H, 5·7%; equiv. (tetrabasic), 88].

The crude methyl ester, prepared from the above acid (77 mg.) and ethereal diazomethane, was passed through alumina (1 × 1·5 cm.) in ether. Fractional crystallisation of the recovered gum (77 mg.) by dilution of an ethereal solution with light petroleum (b. p. 40—60°) gave *A*, needles (48 mg.), and *B*, a gum. Crystallisation of *A* from ether–light petroleum (b. p. 60—80°) gave long needles of α-*methyl* 3 : 5-*dimethoxycarbonyl*-6-(2-*methoxycarbonyl*-6-*methylphenyl*)-3-*methylhexanoate* (VII; R = Me, R′ = CO_2Me), m. p. 83—84°, $[\alpha]_D^{23}$ −6° ± 3° (*c* 1·65 in EtOH) (Found: C, 61·9; H, 6·8; OMe, 30·1. $C_{21}H_{28}O_8$ requires C, 61·75; H, 6·9; OMe, 30·4%).

Repeated recrystallisation of *B* from ether–light petroleum at 0° gave the β-*ester* (21 mg.), small needles, m. p. 47—48°, $[\alpha]_D^{23}$ +12° ± 3° (*c* 1·25 in EtOH) (Found: C, 61·8; H, 7·1; OMe, 29·6%). A mixture of the α- and β-ester had m. p. 50—70°. They could not be interconverted by seeded crystallisation, and the m. p.s were not depressed by mixture with the synthetic α- and β-racemate respectively.[11] The infrared spectra of the natural esters and the corresponding synthetic racemates were identical in carbon tetrachloride.

Oxidation of the Keto-acid (V; R = R′ = H).—(1) A mixture of the acid (700 mg.), potassium permanganate (3·88 g., 15 atom-equiv. of O), magnesium nitrate hexahydrate (7·0 g.), and water (100 ml.) was heated at 80—85° with stirring until the permanganate was consumed and gas evolution ceased (20 min.). After cooling, the precipitate was filtered off and washed with water and dilute aqueous ammonia. Recovery of the product in ether from the combined acidified filtrates gave a gum (0·53 g.). Extraction of the gum with chloroform (*ca.* 4 ml.) gave a semi-solid residue (*A*) (0·15 g.) and a soluble gum (0·3 g.) (*B*). Material *A* was dissolved in a little ether and diluted with chloroform, giving crystals (63 mg.) which were washed with ether. The product (44 mg.), m. p. 181—187°, crystallised from saturated aqueous potassium acetate

solution in glistening flakes (25 mg.). Recrystallisation from water gave potassium benzene-1 : 2 : 3-tricarboxylate, identical (infrared spectrum) with an authentic specimen. The ether and ether–chloroform mother-liquors from *A* were evaporated, giving a gum *C* (73 mg.).

This gum *C* (60 mg.) was spotted on to Whatman's no. 3 MM. paper in 31 spots. The paper was developed for 20 hr. in the phenol–water–formic acid solvent system of Opieńska-Blauth, Saklawska-Szmonowa, and Kański.[17] Very light spraying with bromophenol-blue revealed spots with the R_F values listed below [values for reference acids (100 μg.) in parentheses]: (1) 0·45 (benzene-1 : 2 : 3-tricarboxylic acid and tricarballylic acid, 0·45); (2) 0·54 (β-methyltricarballylic acid 0·55); (3) 0·64; (4) 0·71 (3-methylphthalic acid, 0·71); (5) 0·87. (The crude oxidation product gave an additional weak spot with R_F 0·3, corresponding to oxalic acid.) The spots were cut out and each series was extracted with sodium hydrogen carbonate solution and water. The extracts were concentrated, acidified, and continuously extracted with ether for 22 hr.

Product (1) (9 mg.) was dissolved in ether, filtered from yellow material, and allowed to evaporate, giving crystals, m. p. 182—192° not depressed on admixture with benzene-1 : 2 : 3-tricarboxylic acid. Product (2) (3·5 mg.) was dissolved successively in a little acetone and ether, yellow material being filtered off. Slow evaporation of the ethereal solution gave prisms which were washed with ether and crystallised by dilution of an ethereal solution with carbon tetrachloride, giving (i) prisms, m. p. 157—160° (0·4 mg.), and (ii) prisms, m. p. 151—157° (1·9 mg.). Product (i) recrystallised as prisms, m. p. 158—161°, identified as β-methyltricarballylic acid by mixed m. p. and infrared spectrum.

Product (4) (3 mg.) was combined with a similar fraction (2·8 mg.) from the following experiment. Heating at 100—140°/760 mm. gave a sublimate (1·6 mg.) consisting of long needles, m. p. 110—112°, of 3-methylphthalic anhydride, identical (infrared spectrum) with an authentic specimen.

Products (3) (3 mg.) and (5) (11 mg.) were intractable.

Material *B* was sublimed at 135°/10^{-2} mm. for 2 hr. and the sublimate (104 mg.) in potassium hydroxide was extracted with ether. Recovery of the acidic fraction in ether gave a gum which was heated at 120°/700 mm. for 28 min. and then sublimed at 100—130°/10^{-2} mm., giving a solid (55 mg.). The ether-soluble portion was resublimed at 90°/10^{-2} mm., giving crystals (27 mg.), m. p. 80—100°. Three crystallisations from light petroleum (b. p. 80—100°) gave needles of 3-methylphthalic anhydride m. p. and mixed m. p. 111—114° (Found: C, 66·3; H, 3·8. Calc. for $C_9H_6O_3$: C, 66·7; H, 3·7%).

(2) The acid (143 mg.) was oxidised with magnesium nitrate hexahydrate (770 mg.) and potassium permanganate (420 mg., 8 atom-equiv. of O) in water (5 ml.) for 30 min. at 70° until the reagent was consumed and no more gas was evolved. Of the gummy product (0·12 g.), isolated as described above, 108 mg. was applied to Whatman's no. 3 MM. paper in 54 spots. Development in the same way as before gave spots with the following R_F values: (1) 0·30; (2) 0·46; (3) 0·54; (4) 0·70; (5) 0·87 from which gums were isolated; (2) 3·3 mg.; (3) 1·7 mg.; (4) 2·8 mg.; (5) 43·2 mg.

Crystallisation of fraction (3) from ether–carbon tetrachloride gave prisms (0·8 mg.), m. p. 158—160°, identified as β-methyltricarballylic acid. Fraction (4) was added to a similar fraction from the preceding experiment (see above).

β-Methyltricarballylic Acid.—The acid [18] crystallised from ether–light petroleum (b. p. 40—60°) or from ether–carbon tetrachloride in prisms, m. p. 166—167·5° (lit., m. p. 156—158°,[18] 162—164° [19]) (Found: C, 44·2; H, 5·2. Calc. for $C_7H_{10}O_6$: C, 44·2; H, 5·3%), $\nu_{max.}$ in the double-bond stretching region at 1738, 1712, and 1650 cm.$^{-1}$ and carboxylic acid hydroxyl absorption at ~3100 – ~2500 cm.$^{-1}$. The anhydride crystallised from chloroform in prisms, m. p. 138—140° (Found: C, 48·5; H, 4·6. Calc. for $C_7H_8O_5$: C, 48·8; H, 4·7%); $\nu_{max.}$ (C=O) 1850, 1780, and 1706 cm.$^{-1}$.

Chromatography of the acid on Whatman's no. 3 MM. paper and recovery by the method described for the degradation products (above) resulted in a 68% yield of material of m. p. 155—158°, raised to 160—162° by crystallisation from ether–carbon tetrachloride.

A mixture of the acid (190 mg.), potassium permanganate (948 mg., 9 atom-equiv. of O), and magnesium nitrate hexahydrate (1·80 g.) in water (5·0 ml.) was stirred at 80—85° for 1 hr.

[17] Opieńska-Blauth, Saklawska-Szymonowa, and Kański, *Nature*, 1951, **168**, 511.
[18] Jeger, Rüegg, and Ruzicka, *Helv. Chim. Acta*, 1947, **30**, 1294.
[19] Hope, *J.*, 1912, 892.

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After destruction of the excess of oxidant with ethanol, the crude product (70 mg.) was isolated as described for the degradative experiments (above). 500 μg. were spotted on Whatman's no. 1 paper and developed in the usual way, giving four spots, with R_F 0·24 (trace, tails), 0·46 (20—30%) 0·58 (40—60%), and 0·67 (5—10%), and corresponding to oxalic acid (0·24 tails), tricarballylic acid (0·47), and starting material (0·57). The fourth spot was not identified but may represent the spot (R_F 0·64) which arises in the first degradative oxidation described above.

3-*Methylphthalic Acid.*—(i) Oxidation of 4-methylindan-1-one (1·00 g.) with dilute nitric acid [20] gave a gum which was heated at 160°/760 mm. for 15 min. Repeated sublimation at at 75—90°/10^{-2} mm. gave 3-methylphthalic anhydride (198 mg.), m. p. 104—111°. The free acid crystallised from ethyl acetate–light petroleum in needles (78 mg.), m. p. 151—152° (decomp.) (Found: C, 59·8; H, 4·65. Calc. for $C_9H_8O_4$: C, 60·0; H, 4·5%).

(ii) The indanone (588 mg.), potassium permanganate (1·234 g.), and magnesium nitrate hexahydrate (3·1 g.) in water (10·0 ml.) were heated at 75—85° (stirring) until gas evolution ceased and the oxidant was consumed. Filtration and recovery of the neutral fraction in ether gave starting material (353 mg.). Acidification of the aqueous fraction and recovery of the acidic product in ether followed by sublimation as described above gave 3-methylphthalic anhydride (51 mg.), m. p. 113—115° [from light petroleum (b. p. 80—100°)] (Found: C, 66·4; H, 3·9. Calc. for $C_9H_6O_3$: C, 66·7; H, 3·7%).

2 : 2-*Dimethylindane*-1 : 3-*dione.*—2 : 2-Dimethylindan-1-one (533 mg.), potassium permanganate (1·06 g.), and magnesium nitrate hexahydrate (1·95 g.) in water (8·5 ml.) were heated at 60—75° (stirring) for 4 hr. Filtration and recovery of the neutral product (476 mg.) in ether afforded 2 : 2-dimethylindane-1 : 3-dione (200 mg.), plates, m. p. 104—105° [from light petroleum (b. p. 40—60°)] (Found: C, 75·95; H, 5·8. Calc. for $C_{11}H_{10}O_2$: C, 75·8; H, 5·8%).

We are indebted to Dr. L. A. Duncanson for the infrared spectra and to Messrs. T. J. Ashman, P. J. Suter, and G. Ward for technical assistance.

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[20] Young, *Ber.*, 1892, **25**, 2102.

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514. *Gibberellic Acid. Part VIII.*[1] *Synthesis of Methyl* (±)-α- *and* -β-3 : 5-*Dimethoxycarbonyl*-6-(2-*methoxycarbonyl*-6-*methylphenyl*)-3-*methylhexanoate.*

By A. Morrison and T. P. C. Mulholland.

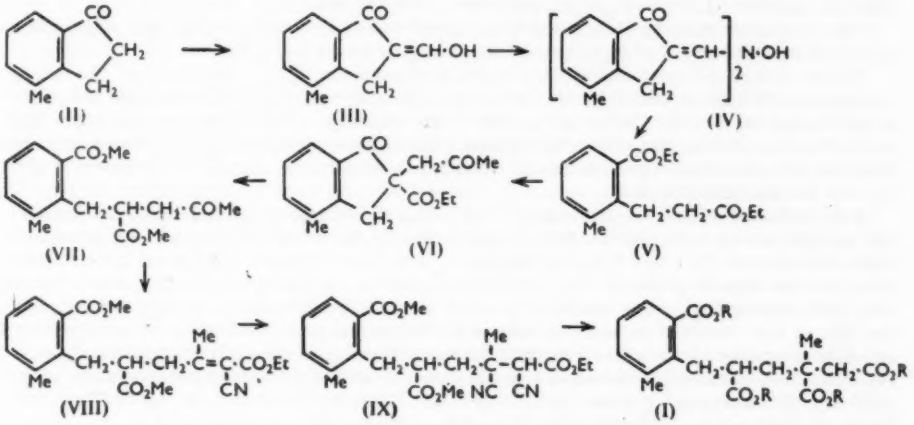
The structures methyl α- and β-3 : 5-dimethoxycarbonyl-6-(2-methoxycarbonyl-6-methylphenyl)-3-methylhexanoate assigned to products obtained by degradation of gibberic acid have been confirmed by the synthesis of their racemates.

Stepwise degradation [1] of gibberic acid has been shown to yield a tetracarboxylic acid, from which two crystalline methyl esters $C_{21}H_{28}O_8$ were obtained. The formation of the two esters, which differed in optical rotatory power, was considered to be due to racemisation of one of two centres of asymmetry during the formation of the acid. The structure (I; R = H) proposed for the acid [1] has been confirmed by the synthesis of racemates of both methyl esters.

4-Methylindan-1-one (II) was converted into 2-formyl-4-methylindan-1-one (III) which with hydroxylamine hydrochloride [2] gave the disubstituted hydroxylamine (IV). Chakravarti [2] considered this compound to be the 2-cyano-derivative but comparison of its

[1] Part VII, Cross, Grove, MacMillan, and Mulholland, preceding paper.
[2] Chakravarti, *J. Indian Chem. Soc.*, 1943, **20**, 393.

properties with those of related compounds [3] showed that it was the disubstituted hydroxylamine. Hydrolysis and esterification then gave ethyl β-(2-ethoxycarbonyl-6-methylphenyl)propionate (V) which on treatment with sodium followed by bromoacetone was converted into ethyl (±)-2-acetonyl-4-methyl-1-oxoindane-2-carboxylate (VI).



Attempts to condense the last compound with ethyl cyanoacetate failed even under vigorous conditions; [4] it was therefore hydrolysed and the product esterified, to give the methyl ester (VII) which condensed satisfactorily. Addition of potassium cyanide across the ethylenic bond of the product (VIII), followed by hydrolysis of the resulting dinitrile (IX), gave the required acid (I; R = H).

Methylation of this acid gave a mixture which was separated into methyl (±)-α-3 : 5-dimethoxycarbonyl-6-(2-methoxycarbonyl-6-methylphenyl)-3-methylhexanoate, m. p. 78—80°, and the (±)-β-isomer, m. p. 36—38°, from which the corresponding tetracarboxylic acids (I; R = H), m. p. 202—205° and 176°, respectively, were prepared by hydrolysis. The synthetic esters did not depress the m. p.s of the corresponding (−)-α-, m. p. 83—84°, and (−)-β-ester, m. p. 46—48°, obtained by degradation [1] and were shown to be racemates of the natural compounds by comparison of their infrared spectra in carbon tetrachloride solution.

Experimental

M. p.s are corrected. Microanalyses are by Messrs. W. Brown and A. G. Olney. Alumina for chromatography and absorption spectra were obtained as described previously.[5]

4-Methylindan-1-one (with Mr. P. J. Suter).—β-*o*-Tolylpropionic acid (1·00 g.) was covered with hydrogen fluoride and kept in a Polythene container for 6 hr. at room temperature. The hydrogen fluoride was allowed to evaporate, the residue was made alkaline with sodium hydrogen carbonate and extracted with ether. The extract was washed with sodium carbonate, then water, dried, and evaporated, giving the indanone (805 mg.) which crystallised from light petroleum (b. p. 60—80°) in needles (690 mg.), m. p. 101—104° (Found: C, 82·2; H, 7·0. Calc. for $C_{10}H_{10}O$: C, 82·2; H, 6·9%) (lit., m. p.'s 96°,[6] 102°,[3] 103—104° [7]).

2-Formyl-4-methylindan-1-one.—4-Methylindan-1-one (9·7 g.) in benzene (80 ml.) was added with shaking during 10 min. to a mixture of ethyl formate (9·7 g.), benzene (50 ml.) and powdered sodium methoxide (from sodium, 3·0 g.), which was cooled in ice. The mixture was kept in ice

[3] Johnson, Anderson, and Shelberg, *J. Amer. Chem. Soc.*, 1944, **66**, 218; Johnson and Shelberg, *ibid.*, 1945, **67**, 1745.
[4] Cope, Hofmann, Wyckoff, and Hardenbergh, *ibid.*, 1941, **63**, 3452; Cragoe, Robb, and Sprague, *J. Org. Chem.*, 1950, **15**, 381.
[5] Mulholland and Ward, *J.*, 1954, 4676.
[6] Plattner and Wyss, *Helv. Chim. Acta*, 1940, **23**, 907.
[7] Mercer and Robertson, *J.*, 1936, 288.

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for 15 min., then at room temperature overnight, and was then shaken with ice-water. Ether was added and the combined aqueous layer and water washings of the organic layer were washed with ether and acidified with ice-cold dilute hydrochloric acid. The *formyl derivative* (11·1 g.), m. p. 166—168° (decomp.), was filtered off and used for further work without purification. A specimen crystallised from benzene in pale yellow prisms, m. p. 168—170° (decomp.) (Found: C, 75·8; H, 5·95. $C_{11}H_{10}O_2$ requires C, 75·8; H, 5·8%).

The compound has been obtained in crude form [2] but an attempt to repeat this preparation, which involved the use of a large excess of sodium, gave a very low yield.

NN-*Di*-(4-*methyl*-1-*oxo*-2-*indanylidenemethyl*)*hydroxylamine* (IV).—Reaction of the above compound with hydroxylamine hydrochloride in acetic acid [2] gave the hydroxylamine derivative as an orange-red powder (85%), m. p. 220—222° (decomp.), which was not purified. The product was soluble in, and gave a blue colour with, dilute aqueous sodium hydroxide and was therefore not the simple cyano-ketone.[2] It appeared to form an acetate (cf. Johnson *et al.*[3]) but this was not obtained pure.

β-(2-*Carboxy*-6-*methylphenyl*)*propionic Acid*.—The above hydroxylamine derivative (33·0 g.) and hydroxylamine hydrochloride (6·8 g.) were heated under reflux with aqueous 3% potassium hydroxide solution (7 l.) for 12 days in nitrogen. The volume was reduced to *ca.* 2 l. by distillation at atmospheric pressure, and the residual solution was washed with ether and acidified with hydrochloric acid. The combined product obtained by filtration and ether-extraction of the filtrate was dissolved in aqueous sodium hydrogen carbonate, recovered by acidification, and then crystallised from water (charcoal), giving pale yellow needles of the acid (21·2 g.), m. p. 167—169°. A specimen, sublimed *in vacuo* and recrystallised, formed colourless needles, m. p. 173—174° (Chakravarti [2] gives m. p. 172°) (Found: C, 63·6; H, 5·75. Calc. for $C_{11}H_{12}O_4$: C, 63·45; H, 5·8%), $\lambda_{max.}$ (in EtOH) 232, 277—282 mμ (log ε 3·85, 3·26 respectively).

The diethyl ester [2] distilled as a colourless oil, b. p. 120—121°/10^{-1} mm. (86%).

Ethyl (±)-2-*Acetonyl*-4-*methyl*-1-*oxoindane*-2-*carboxylate* (VI).—The above diethyl ester (22·7 g.) in benzene (120 ml.) was added to powdered sodium (2·37 g.) in benzene (*ca.* 20 ml.) and heated under reflux in nitrogen for 4 hr. After cooling, a solution of bromoacetone (14·2 g.) in benzene (50 ml.) was added at 0° with shaking. The mixture was kept at 0° for 1 hr., at room temperature overnight and then heated under reflux in nitrogen for 15 hr. After cooling, shaking with ice-water, and dilution with ether, the organic fraction was separated, combined with ether washings of the aqueous fraction, washed with water, dried, treated with charcoal, and filtered. Evaporation and treatment of the residual gum with small amounts of ether gave crystals of the sparingly soluble *ketone* (15·4 g.), m. p. 103—108°. Chromatography of the mother-liquor in ether on alumina gave more product (705 mg.). Crystallisation of a specimen from benzene–light petroleum and dilute ethanol gave prisms, m. p. 110—111° (Found: C, 70·2; H, 6·6. $C_{16}H_{18}O_4$ requires C, 70·05; H, 6·6%), $\lambda_{max.}$ (in EtOH) 256, 300 mμ (log ε 4·08, 3·25 respectively).

The *semicarbazone*, prepared in pyridine, crystallised from ethanol in needles, m. p. 183—185° (decomp.) (Found: C, 61·55; H, 6·5; N, 12·2. $C_{17}H_{21}O_4N_3$ requires C, 61·6; H, 6·4; N, 12·7%).

Attempts to condense the ketone with ethyl cyanoacetate failed.

(±)-2-(2-*Carboxy*-6-*methylbenzyl*)-4-*oxopentanoic Acid* (CO_2H = 1).—A mixture of the above ketone (16·1 g.) and a 20% solution of potassium hydroxide in 50% aqueous ethanol (805 ml.) was heated under reflux for 3 hr. The ethanol was removed *in vacuo* and the residue was washed with ether, treated with charcoal, filtered, and acidified with hydrochloric acid. After storage overnight at 0° the *keto-acid* (9·45 g.; m. p. 171—174°) was filtered off, and a further crop (274 mg.) was recovered from the mother-liquor by ether-extraction followed by crystallisation from ethyl methyl ketone–light petroleum (b. p. 60—80°). A specimen recrystallised as needles, m. p. 173—174° [Found: C, 63·5; H, 6·05%; equiv., 136. $C_{14}H_{16}O_5$ requires C, 63·6; H, 6·1%; equiv. (dibasic), 132], $\lambda_{max.}$ (in EtOH) 232, 282—283 mμ (log ε 2·77; 2·11 respectively). The yellow 2 : 4-*dinitrophenylhydrazone*, crystallised from dilute acetic acid, had m. p. 248—250° (Found: C, 54·4; H, 4·6; N, 12·5. $C_{20}H_{20}O_8N_4$ requires C, 54·05; H, 4·5; N, 12·6%). The *methyl ester* (VII), prepared with ethereal diazomethane, crystallised from dilute methanol in needles, m. p. 49—51°, but consistent analyses were not obtained. Recrystallisation from ether–light petroleum (b. p. 40—60°) gave prisms, m. p. 50—52° (Found: C, 65·9; H, 7·1; OMe, 20·7. $C_{16}H_{20}O_5$ requires C, 65·7; H, 6·9; 2OMe, 21·2%).

Methyl (±)-3 : 5-*Dimethoxycarbonyl*-6-(2-*methoxycarbonyl*-6-*methylphenyl*)-3-*methylhexanoate*

(I; R = Me).—(i) A mixture of the above methyl ester (7·00 g.), ethyl cyanoacetate (4·05 g.), acetic acid (2·31 g.), and ammonium acetate (0·50 g.) in benzene (40 ml.) was heated under reflux for 20 hr. in an apparatus fitted with a Dean and Stark [8] water separator. After each 4-hr. period more ammonium acetate (4 × 0·4 g.) was added. The cooled mixture was diluted with ether, washed with water, dried, and evaporated, giving an oil (10·1 g.). Distillation *in vacuo* gave unchanged ethyl cyanoacetate (bath-temp. up to 140°/10^{-2} mm.) and a very viscous yellow oil (7·71 g.) of b. p. 176—184°/15 × 10^{-2} mm. consisting essentially of ethyl (±)-2-cyano-5-methoxycarbonyl-6-(2-methoxycarbonyl-6-methylphenyl)-3-methylhex-2-enoate (VIII).

(ii) The above nitrile (7·70 g.) in ethanol (50 ml.) was treated slowly at 10° with potassium cyanide (2·6 g.) in water (20 ml.). The mixture was kept at room temperature for 1 hr., heated under reflux for 30 min., cooled to 0—5°, and acidified with dilute hydrochloric acid (70 ml.; 1 : 1). The crude ethyl (±)-2 : 3-dicyano-5-methoxycarbonyl-6-(2-methoxycarbonyl-6-methylphenyl)hexanoate (IX) (6·9 g.) was recovered in ether as a gum, which was not purified.

(iii) The above dinitrile (6·9 g.) and 50% sulphuric acid (300 ml.) were heated under reflux in a stream of nitrogen until evolution of carbon dioxide ceased (50 hr.). On cooling, an oil separated which solidified. After removal of a globule of tar (*ca.* 0·1 g.) the mixture was extracted with ether. Recovery from the extract gave (±)-α- and -β-3 : 5-dicarboxy-6-(2-carboxy-6-methylphenyl)-3-methylhexanoic acid (I; R = H) as a pale yellow gum (6·8 g.). Pure specimens were prepared from the methyl esters (see below).

(iv) Esterification of the above acid (6·8 g.) with diazomethane gave a neutral yellow gum (6·0 g.) which was chromatographed on alumina (18 × 2·5 cm.) in ether and eluted with the same solvent (150 ml. fractions) until the last fraction gave only 3 mg. on recovery. The product (5·4 g.) crystallised from ether–light petroleum (b. p. 40—60°), giving a sticky solid (3·4 g.), m. p. 48—64°, and a gum which was distilled, b. p. 175—185°/10^{-1} mm. (1·58 g.). Recrystallisation of the solid product from ether–light petroleum and then from light petroleum (b. p. 60—80°) gave needles (1·83 g.) of methyl (±)-α-3 : 5-dimethoxycarbonyl-6-(2-methoxycarbonyl-6-methylphenyl)-3-methylhexanoate (I; R = Me), m. p. 78—79°, raised to 79—80° by further crystallisation (Found: C, 61·85; H, 7·0; OMe, 30·0. $C_{21}H_{28}O_8$ requires C, 61·75; H, 6·9; 4OMe, 30·4%).

After the recovery of a small amount of the α-ester from the crystallisation mother-liquors the gummy fractions were combined and separated from most of a ketonic impurity with Girard's reagent T in methanol (Girard's reagent P or chromatography on alumina was ineffective). The material recovered was only weakly ketonic to Brady's reagent. Colour was removed by passage of an ethereal solution through alumina (16 × 1·4 cm.). The gum (2·59 g.) which was recovered crystallised on addition of light petroleum (b. p. 40—60°) to an ethereal solution at −10° to 0°. Three crops of crystals (2·02 g.), m. p. range 35—50°, were combined and fractionally crystallised, giving the (±)-β-*ester* as small needles (180 mg.), m. p. 34—36° (Found: C, 61·7; H, 6·9; OMe, 29·1%). From the mother-liquors two further batches of less pure material were obtained: (*a*) 984 mg., m. p. 39—42°; (*b*) 124 mg., m. p. 37—40°. The infrared spectra of the (±)-α- and -β-racemate in solution in carbon tetrachloride were identical with those of the α- and β-ester respectively obtained from gibberic acid.

Hydrolysis.—A solution of the above (±)-α-ester (400 mg.) in 6% ethanolic potassium hydroxide (10 ml.) was heated under reflux for 2 hr. The potassium salt which separated was filtered off, washed with ethanol, and dissolved in water. Acidification of the solution with hydrochloric acid followed by recovery of the product in ether gave (±)-α-3 : 5-*dicarboxy*-6-(2-*carboxy*-6-*methylphenyl*)-3-*methylhexanoic acid* (I; R = H) (215 mg.), m. p. 202—204° (decomp.). This separated from ethyl methyl ketone–light petroleum (b. p. 60—80°) as an amorphous white powder (155 mg.), m. p. 204—205° (decomp.) [Found: C, 58·2; H, 5·9%; equiv., 88. $C_{17}H_{20}O_8$ requires C, 57·95; H, 5·7%; equiv. (4 CO_2H), 88].

The (±)-β-ester (500 mg.), hydrolysed in the same way, gave the (±)-β-*acid* as an amorphous white powder (202 mg.), m. p. 176° (decomp.) (Found: C, 58·0; H, 5·9%; equiv., 84).

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[8] Dean and Stark, *Ind. Eng. Chem.*, 1920, **12**, 486.

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515. *Complexes of Bivalent and Tervalent Cobalt with a Terdentate and a Quadridentate Amine.*

By G. A. Barclay and A. K. Barnard.

2 : 2′-Diaminodiethylamine (dn) with cobaltous salts yields compounds Co dnX_2 and Co dn_2X_2; their magnetic moments indicate that no spin-pairing occurs. Both types are readily oxidised to tervalent cobalt complexes, Co dn_2X_2, which are diamagnetic and, therefore, spin-paired and octahedral. The compound Co dn$(NO_2)_2$ is also spin-paired and octahedral. This behaviour is compared with that of a tritertiary arsine which causes electron-pairing in all cases and forms quinquecovalent complexes with cobaltous halides.

2 : 2′ : 2″-Triaminotriethylamine forms spin-free compounds Co trenX_2 with bivalent cobalt salts. Co tren$(OH)_2Cl$ and Co tren$(SCN)_2,H_2O$ are diamagnetic compounds, indicating the usual spin-paired type complex of tervalent cobalt.

As part of an investigation concerned with the effects of multidentate chelate groups and of the electronegativity of the donor atom on the stereochemistry and bond type of transition-metal complexes, we have studied the compounds of cobalt salts with 2 : 2′-diaminodiethylamine and 2 : 2′ : 2″-triaminotriethylamine. Although a few complexes of these amines [1,2,3] have been prepared and the susceptibility of one of them reported,[4] no systematic magnetic studies have been carried out.

Table 1.

Valency	Stereochem.	Bonding orbitals	No. of unpaired electrons	Magnetic moments * Calc.	Found
II	Planar	$3d4s4p^2$	1	1·73	2·1—2·9
II	Octahedral	$3d^24s4p^2$	1 †	1·73	1·7—2·0
II	Tetrahedral	$4s4p^3$	3	3·87	4·3—4·8
II	Octahedral	$4s4p^24d^2$	3	3·87	4·8—5·2
III	Octahedral	$3d^24s4p^3$	0	0·00	Diamagn.
III	Octahedral	$4s4p^34d^2$	4	4·90	4·26

* In Bohr magnetons. The calculated moments are spin-only values. † See below.

Recently the relation between bond type and electronegativity of the donor atom has received much attention.[5,6] Calculations of overlap integrals for the use of 3*d*- and 4*d*-orbitals by metals of the first transition series support the conclusions that the more electronegative donor atoms should favour the use of octahedral $4s4p^34d^2$-bonding orbitals, while the less electronegative donors should favour $3d^24s4p^3$-orbitals.[7] In the latter case it is generally necessary for electron-pairing to occur in order to free sufficient 3*d*-orbitals for bonding; complexes of this type are therefore known as "spin-paired," but with the former type such electron-pairing is not required and the complexes are "spin-free." [8] This subject has been reviewed from the standpoint of the ligand-field theory.[9] It is therefore of interest to compare the complexes of ligands with donor atoms of high electronegativity, *e.g.*, nitrogen, with those of lower electronegativity, *e.g.*, arsenic.

The relation between the valency states and the stereochemistry of cobalt in its co-ordination compounds with their magnetic moments is shown in Table 1 (cf. Figgis and

[1] Breckenridge, *Canad. J. Res.*, 1948, **26**, *B*, 11; Mann and Pope, *J.*, 1926, 483.
[2] Mann, *J.*, 1934, 471.
[3] Mann, *J.*, 1929, 409.
[4] Cox and Webster, *Z. Krist.*, 1935, **92**, 478.
[5] Taube, *Chem. Rev.*, 1952, **50**, 69.
[6] Burstall and Nyholm, *J.*, 1952, 3570.
[7] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332; Craig, *Rev. Pure Appl. Chem.* (*Australia*), 1954, **4**, 4.
[8] Nyholm, Reports of the Xth Solvay Council, Brussels, May, 1956.
[9] Griffiths and Orgel, *Quart. Rev.*, 1957, **11**, 381; Gillespie and Nyholm, *ibid.*, p. 339.

Nyholm [10]). With bivalent cobalt the use of the magnetic moment to determine the number of unpaired electrons on the metal atom fails to distinguish between tetrahedral and octahedral complexes of the spin-free type, and between planar and octahedral co-ordination in spin-paired complexes. According to Nyholm,[11] the magnitude of the orbital contribution to the magnetic moment (the amount by which the moment exceeds that calculated from the "spin-only" formula) may be diagnostic of the stereochemistry of the metal. In the case of spin-free complexes of bivalent cobalt, a field of tetrahedral symmetry should cause a greater quenching of the orbital contribution than one of octahedral symmetry. These conclusions are found to be true in practice and from a study of the magnetic moments of a large number of compounds it has been postulated that the moments of tetrahedral complexes are generally lower than 4·8 B.M., while those of octahedral complexes lie in the range 4·8—5·2 B.M.[10,11]

With spin-paired complexes the conclusions are similar. Planar complexes have one unpaired electron in a 3*d*-orbital where there would be expected to be a significant orbital contribution; in agreement, the moments of such compounds are found to lie in the range 2·1—2·9 B.M. (spin-only value 1·73 B.M.). With octahedral complexes the problem is more difficult. If the bonding orbitals are $3d^24s4p^3$ it is necessary to remove one electron († in Table 1) from a 3*d*-orbital in order to free two such orbitals for bonding. The most energetically favourable orbital for this electron is now the 5*s*, where, since the angular momentum is zero, the orbital contribution should be zero; in fact, the observed moments for such complexes (1·7—2·0 B.M.) lie close to the spin-only value. However, the Referees

TABLE 2. *Magnetic moments of powdered samples at* 20°.

Complex	Colour	$10^6\chi_M$	Diamag.* (corr.)	$10^6\chi'_M$	μ (B.M.)
Co dnCl_2	Blue	9390	114	9504	4·74
Co dnBr_2	Blue	9140	132	9272	4·68
Co $dn_4Cl_2.H_2O$	Violet	11,510	194	11,704	5·26
Co dn_2Cl_2	Violet-blue	11,530	181	11,711	5·26
Co dn_2I_2	Purple	11,040	236	11,276	5·16
Co $dn_2(ClO_4)_2$	Purple	9710	199	9909	4·84
Co dn_2I_2	Brown	—†	—	—	0·00
Co $dn_3(ClO_4)_2$	Brown	—†	—	—	0·00
Co $dn(NO_3)_2$	Yellow-brown	—†	—	—	0·00
Co tren$(SCN)_2$	Olive-green	9520	157	9677	4·78
Co trenI_2	Blue	9360	197	9557	4·75
Co tren$(OH)_2Cl$	Brown	—†	—	—	0·00
Co tren$(SCN)_2SCN,H_2O$	Red	—†	—	—	0·00

* These values are calculated from constants given by Selwood; [13] the diamagnetism of the metal has been ignored in all cases. † The method of measurement did not permit the precise determination of diamagnetic susceptibilities.

have kindly pointed out that the alternative view is that the electron remains in the $3dz^2$ orbital, where it would repel two donor atoms in *trans*-positions. This would imply that the bonding orbitals were of two types, *viz.*, $3d4s4p^2$ square planar and two longer $4p4d$ collinear bonds perpendicular to the plane. This view has not been experimentally substantiated for octahedral spin-paired bivalent cobalt complexes, but an *X*-ray study [12] of [Pd(diarsine)$_2$I$_2$] (where there would be expected to be two electrons in the $4dz^2$ orbital) has shown that the two Pd–I distances are longer than expected for $4d^25s5p^3$-bonding.

Our experimental results for the complexes of bivalent and tervalent cobalt with 2 : 2′-diaminodiethylamine (dn) and 2 : 2′ : 2″-triaminotriethylamine (tren) are summarised in Table 2. The complexes of bivalent cobalt are very readily oxidised in solution and it is therefore necessary to exclude air during their preparation. Solutions of the ligand and

[10] Figgis and Nyholm, *J.*, 1954, 12.
[11] Nyholm, *Quart. Rev.*, 1953, **7**, 402; Klyne, "Progress in Stereochemistry," Butterworths London, 1955, p. 333.
[12] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.
[13] Selwood, "Magnetochemistry," Interscience Publ. Inc., New York, 1943, p. 52.

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cobalt salt in alcohol were mixed and the complex was filtered off in an all-glass apparatus which allowed the whole operation to be carried out in an atmosphere of nitrogen.

The tervalent complexes with both ligands are diamagnetic; hence $3d^2 4s 4p^3$ octahedral orbitals of the metal are probably involved in the bonding. The conductivities in aqueous solution of Co dn_2I_3 (350 mho) and Co $dn_2(ClO_4)_3$ (339 mho) indicate that they are behaving as ter-univalent electrolytes. Unless water molecules are co-ordinated with the ion in solution, the diaminodiethylamine acts as a terdentate ligand in these compounds. Similarly as [Co tren$(SCN)_2$]SCN and [Co tren$(OH)_2$]Cl behave as uni-univalent electrolytes in water, it seems likely that the triaminotriethylamine is bonded to the cobalt atom through each of its four amino-groups. It is assumed, therefore, that the two ligands act as terdentate and quadridentate donors respectively in the other complexes isolated.

The compounds of bivalent cobalt are all of the spin-free type. Those with empirical formula Co dnX_2 may be formulated either as complexes containing tetrahedrally co-ordinated cobalt(II) [Co dnX]X, or as dimeric compounds, [Co dn_2][CoX_4]. Their magnetic moments (4·7 B.M.) do not distinguish between these two structures; the former should have a moment somewhat lower than 4·8 B.M., while the mean moment of the two cobalt atoms in the second formulation should be the mean of the values for Co $dn_2(ClO_4)_2$ (4·84 B.M.) and for $[CoX_4]^{2-}$ (4·76 B.M., X = Cl; 4·62 B.M., X = Br), *viz.*, 4·8 and 4·7 B.M. for the chloride and bromide respectively. The compounds Co dn_2X_2 (X = Cl, I, ClO_4) have magnetic moments in the range 4·8—5·3 B.M. and are probably octahedral complexes involving $4s4p^34d^2$-orbitals of the cobalt atom.

The behaviour of the tri-tertiary arsine, $CH_3{\cdot}As(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}AsMe_2)_2$ with cobaltous salts [14] forms an interesting contrast with the corresponding compound, diaminodiethylamine, containing donor atoms of greater electronegativity. Thus, the triarsine causes electron-pairing in all cases while the amine fails to do so. In nitrobenzene solution the compounds containing one triarsine group per cobalt atom are non-electrolytes and are probably quinquecovalent, at least in this solvent. The magnetic moments indicate one unpaired electron; hence, the 3*d*-orbitals of the cobalt atom are involved in bonding, probably forming $3d4s4p^3$-hybrid orbitals and a square-pyramidal arrangement of ligand atoms. Although the bis(terdentate)cobalt(II) complexes with both ligands are octahedral, the triarsine causes electron-pairing whereas the diaminodiethylamine compounds are of the spin-free type. All these bivalent cobalt compounds are readily oxidised in solution to complexes of tervalent cobalt.

Non-ionic complexes of tervalent cobalt of the type Co(terdentate)X_3 were isolated more easily with the triarsine than with diaminodiethylamine. With the latter, Co $dn(NO_2)_3$ was the only compound of this type obtained. However, while diaminodiethylamine forms the complexes Co dn_2X_2 (X = I^- or ClO_4^-), no similar compound containing two triarsine groups is obtained. Both ligands, in common with practically all others, form diamagnetic complexes of tervalent cobalt which are spin-paired and octahedral.

From the reaction of triaminotriethylamine with cobaltous salts, the compounds Co trenX_2 (X = SCN or I) were the only two isolated. The values of their magnetic moments (4·8 B.M.) do not distinguish between the two possible stereochemical arrangements (tetrahedral or octahedral) but indicate that the complexes are of the spin-free type.

Experimental

Commercial diaminodiethylamine was purified by distillation under reduced pressure (b. p. 93—94°/17 mm.).

2 : 2′-*Diaminodiethylaminecobalt*(II) *Chloride*.—Cobalt chloride hexahydrate (1·0 g.) in air-free absolute alcohol (20 ml.) was treated with diaminodiethylamine (0·5 g.) in air-free absolute alcohol (10 ml.). A blue solid quickly separated from the deep blue solution. The *chloride*

[14] Barclay and Nyholm, *Chem. and Ind.*, 1953, 378, also unpublished results; cf. Barclay, *Rev. Pure Appl. Chem.* (*Australia*), 1954, **4**, 77.

was filtered off under nitrogen, washed with air-free alcohol–ether, and dried in a vacuum-desiccator (Found: C, 20·4; H, 5·6; Cl, 30·2. $C_4H_{13}Cl_2N_3Co$ requires C, 20·6; H, 5·6; Cl, 30·4%). The mol. conductivity in M/1000-aqueous solution at 22° = 197 mho.

Similarly prepared were the analogous salts:

Bromide (1·4 g. from 1·55 g. of cobalt bromide), blue (Found: C, 14·8; H, 4·3; Br, 49·9. $C_4H_{13}Br_2N_3Co$ requires C, 14·9; H, 4·1; Br, 49·6%), mol. conductivity in M/1000-aqueous solution at 22° = 218 mho.

Chloride (1·8 g. from 1·5 g. of cobalt chloride hexahydrate and 1·3 g. of diaminodiethylamine), violet-blue (Found: C, 28·3; H, 7·9; Cl, 21·0. $C_8H_{26}Cl_2N_6Co$ requires C, 28·6; H, 7·8; Cl, 21·1%), mol. conductivity in M/1000-aqueous solution at 24° = 224 mho.

Chloride monohydrate (1·0 g. from 1·5 g. of cobalt chloride hexahydrate), violet (from 90% aqueous alcohol) (Found: C, 27·0; H, 8·2; Cl, 20·0. $C_8H_{28}OCl_2N_6Co$ requires C, 27·1; H, 8·0; Cl, 20·0%), mol. conductivity in M/2000-aqueous solution at 24° = 224 mho.

Iodide, purple (Found: C, 18·3; H, 4·8; I, 48·7. $C_8H_{26}I_2N_6Co$ requires C, 18·5; H, 5·05; I, 48·9%), mol. conductivity in M/1000-aqueous solution at 23° = 229 mho.

Perchlorate (1·2 g. from 1·5 g. of cobalt perchlorate), purple (Found: C, 20·6; H, 5·5. $C_8H_{26}O_8Cl_2N_6Co$ requires C, 20·7; H, 5·65%), mol. conductivity in M/1000-aqueous solution at 22° = 216 mho.

Bis-(2 : 2′-diaminodiethylamine)cobalt(III) *Iodide*.—The dark brown crystals were prepared by Mann's method [2] (Found: C, 15·3; H, 4·05; I, 59·0. Calc. for $C_8H_{26}I_2N_6Co$: C, 14·9; H, 4·05; I, 58·9%), mol. conductivity in M/2000-aqueous solution at 24° = 350 mho.

Bis-(2 : 2′-diaminodiethylamine)cobalt(III) *Perchlorate*.—The solution containing the $[Co\ dn_2]^{3+}$ ion, prepared from aquopentamminocobalt(III) chloride (4·0 g.) by Mann's method,[2] was poured into a concentrated solution of sodium perchlorate; deep brown crystals of the *perchlorate* were deposited slowly. The complex (2·9 g.) was recrystallised from water (Found: C, 17·0; H, 4·8. $C_8H_{26}O_{12}Cl_2N_6Co$ requires C, 17·05; H, 4·6%) and had mol. conductivity in M/1000-aqueous solution at 23° = 339 mho.

Trinitro-(2 : 2′-diaminodiethylamine)cobalt(III).—This compound was prepared after attempts to obtain complexes of the type $Co\ dnX_3$ (X = Cl, Br, or SCN) had failed. Diaminodiethylamine (7·6 g.) and sodium nitrite (80·0 g.) were dissolved in water (250 ml.), and a solution of cobaltous acetate (18·3 g.) in water (100 ml.) was added. To the ice-cold mixture, hydrogen peroxide (20-vol.; 15 ml.) was added with stirring. The red solution became brown and a yellow-brown solid separated overnight. This mixture was heated with decolorising charcoal and filtered. A solid (5·0 g.) then crystallised at 0°, and was recrystallised from a large volume of hot water containing a few drops of acetic acid. The *complex* (3·5 g.) separated as yellow-brown plates which were moderately soluble in hot water but insoluble in organic solvents (Found: C, 16·1; H, 4·35. $C_4H_{13}O_6N_6Co$ requires C, 16·0; H, 4·4%), mol. conductivity in M/2000-aqueous solution at 23° = 28 mho.

2 : 2′ : 2″-Triaminotriethylamine Trihydrochloride.—The colourless crystals, prepared by the method of Mann and Pope,[15] were purified by recrystallisation from aqueous alcohol.

2 : 2′ : 2″-Triaminotriethylaminecobalt(II) *Thiocyanate*.—Triaminotriethylamine trihydrochloride (0·6 g.) was warmed with 33% sodium hydroxide solution (0·75 ml.) on a water-bath. Absolute alcohol (40 ml.) was added and the precipitated sodium chloride filtered off. The solution was de-aerated by boiling, then added to a solution of cobaltous thiocyanate (0·4 g.) in air-free absolute alcohol (20 ml.). The mixture, which was kept under nitrogen, became green and an olive-green precipitate was formed. The *complex* (0·6 g.) was filtered off quickly, washed with alcohol–ether, and dried in a vacuum-desiccator (Found: C, 30·0; H, 5·4. $C_8H_{18}N_6S_2Co$ requires C, 29·9; H, 5·65%).

2 : 2′ : 2″-Triaminotriethylaminecobalt(II) *Iodide*.—By reaction as for the thiocyanate, triaminotriethylamine trihydrochloride (0·4 g.) gave the *iodide* (0·5 g.) as a blue solid (Found: C, 15·6; H, 3·75. $C_6H_{18}I_2N_4Co$ requires C, 15·7; H, 3·95%).

Dihydroxy-(2 : 2′ : 2″-triaminotriethylamine)cobalt(III) *Chloride*.—Triaminotriethylamine trihydrochloride (0·4 g.) was dissolved in 33% sodium hydroxide solution (0·6 ml.), diluted with water (20 ml.), and warmed on the steam-bath. This solution was added to cobalt chloride hexahydrate (0·4 g.) in water (25 ml.), and filtered air was bubbled through the mixture for 24 hr. The resulting deep crimson solution was poured into a large volume of alcohol, crystals

[15] Mann and Pope, *Proc. Roy. Soc.*, 1925, **109**, *A*, 444.

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being slowly deposited. The *complex* (0·4 g.) was filtered off, washed with alcohol, and air-dried (Found: C, 26·0; H, 7·4; Cl, 12·8. $C_6H_{20}O_2ClN_4Co$ requires C, 26·2; H, 7·3; Cl, 12·9%). It had mol. conductivity in M/1000-aqueous solution at 22° = 142 mho.

Dithiocyanato-(2 : 2′ : 2″-triaminotriethylamine)cobalt(III) *Thiocyanate Monohydrate.*—The brilliant red needles, prepared by Mann's method,[3] were recrystallised twice from a small volume of hot water (Found: C, 27·6; H, 5·1. Calc. for $C_9H_{26}ON_7S_3Co$: C, 27·4; H, 5·05%), mol. conductivity in M/2000-aqueous solution at 22° = 121 mho.

Magnetic Measurements.—The magnetic susceptibilities were determined on the finely powdered solids (*ca.* 10 mg.) in an apparatus of the type described by Blaha.[16] The sensitivity of the microbalance was such as to permit accurate determination of paramagnetic susceptibilities, though the smaller diamagnetic susceptibility of the complexes of tervalent cobalt could not be measured precisely.

Conductivity Measurements.—A conductance bridge with a dip-type cell was used.

We thank the University of Leeds for the award of an I.C.I. Fellowship (to G. A. B.) and the D.S.I.R. for a maintenance grant (to A. K. B.). We are indebted to Professor E. G. Cox for his interest.

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[16] Blaha, *Mikrochemie*, 1952, **39**, 339.

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516. *The Decomposition of Ionised Cyanates in Aqueous Solution. Part II.* Kinetic Studies on the Isomerisation of Alkylammonium Cyanates.*

By P. Johncock, G. Kohnstam, and D. Speight.

The formation of alkylureas from aqueous alkylammonium cyanates is considered to occur by nucleophilic addition of the conjugate amine to cyanic acid. There is no relation between the base strength and the rate, and the results suggest that C–H bonds attached to the nitrogen atom of the amine stabilise the transition state by hyperconjugative electron-release which is relayed to the reaction centre by the inductive mechanism.

Ionised cyanates decompose in water to give *carbonate* † and urea; when alkylammonium ions are present, substituted ureas are also formed. Bearing in mind that the reactants and products will participate in the usual acid–base equilibria, these processes can be represented by the stoicheiometric equations:

$$NCO^- + 2H_2O \rightleftharpoons CO_3^{2-} + NH_4^+ \quad \text{(i)}$$

$$NCO^- + NH_4^+ \rightleftharpoons (NH_2)_2CO \quad \text{(ii)}$$

$$NCO^- + NRR'H_2^+ \longrightarrow NRR'\cdot CO\cdot NH_2 \quad \text{(ii}a\text{)}$$

where R and R′ are alkyl or H. The kinetics of reactions (i) and (ii) were discussed in Part I where it was proposed that a molecule of cyanic acid, and not a cyanate ion, is concerned in each of the various rate-determining steps. There is no reason for supposing that this does not also apply in reaction (ii*a*), and we now report a kinetic study of the isomerisation of some alkylammonium cyanates in water. Some of the present systems

* The paper, *J.*, 1956, 900, by Kemp and Kohnstam, is to be regarded as Part I of this series.

† Throughout this paper the italicised terms *carbonate, cyanate, ammonium,* and *alkylammonium* are used collectively and refer to the total amounts in which these substances can be shown to be present.

were investigated many years ago by Walker and Appleyard,[1] but a repetition of their work seemed desirable since several of their assumptions can no longer be justified. A few of the reactions have also been studied in 98% ethanol,[2] but an interpretation of the results is difficult as we do not know the proportions of the reactants which are in the form of their conjugate acids and bases.*

Rate measurements were carried out at 60·10° on *ca.* 0·05M-aqueous alkylammonium cyanate which had been made slightly alkaline ([OH^-] varied in the range 3×10^{-5} to 5×10^{-4}). The initial ionic strength was adjusted to 0·25 by the addition of potassium nitrate; changes in ionic strength during any one kinetic run were then small enough to permit the use of concentration units in the rate equations. Rate coefficients were obtained from equation 1 which had already been found to predict the rate of formation of urea over a wide range of pH (Part I):

$$d[NRR'\cdot CO\cdot NH_2]/dt = k_1'[NRR'H_2^+][NCO^-] - k_2[NRR'\cdot CO\cdot NH_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The second term gives the rate of the retrograde step, but it was only necessary to determine this for the reactions of the dimethyl and diethyl compounds (see p. 2550) where k_2 was obtained from independent measurements on the alkyl-ureas.

Walker and Appleyard [1] studied the reactions in 0·1M-solutions, no other substances being added. Their data at *ca.* 60° are compared below with the present results, the earlier figures in parentheses (k_1' in sec.$^{-1}$ mole^{-1} l., k_2 in sec.$^{-1}$):

	$NRR'H_2^+$	NH_4^+	$NMeH_2^+$	$NMe_2H_2^+$	$NEtH_2^+$	$NEt_2H_2^+$
$10^3k_1'$	.....	1·250 (2·40)	1·695 (2·23)	3·202 (4·22)	1·116 (1·35)	1·052 (1·50)
10^4k_2	.....	0·262 (0·63)	—	1·15 (12·2)	—	3·65 (24·7)

The smaller values now observed for k_1' are consistent with the neglect of *carbonate* formation by reaction (i) in the previous work (cf. Part I and ref. 3), and with the lower and variable ionic strength of the solutions then employed. It is noteworthy that the discrepancy is greatest for ammonium cyanate, where we would also expect the most *carbonate* formation since the ammonium ion is a considerably stronger acid than its alkyl-substituted derivatives and therefore yields solutions of lower pH.† The other four cations have roughly the same acid strengths, and the earlier values differ from ours by an almost constant factor. It was therefore assumed that the same factor applies to *iso*- and *tert.*-amylammonium ions (which were not studied in the present work) and the corrected data for these species have been included in Table 1 where our main results are summarised. The large discrepancies in the k_2's probably result from the fact that the earlier values were obtained from k_1 at 60° and the equilibrium constant at 100°.

Equation 1 can also be written in the form

$$d[NRR'\cdot CO\cdot NH_2]/dt = k_1[NRR'H][HNCO] - k_2[NRR'\cdot CO\cdot NH_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $k_1 = k_1'K_{Iv}/K_{III}$, $K_{III} = [HNCO][OH^-]/[NCO^-]$ and $K_{Iv} = [NRR'H_2^+][OR^-]/NRR'H$. The values of these equilibrium constants at ionic strength 0·25 are given in the Experimental section (p. 2550). K_{III}, and K_{Iv} for the amines containing branched alkyl groups, are not accurately known at our reaction temperature, and each k_1' is therefore more reliable than the corresponding k_1. However, any error in K_{III} does not affect a

* A change from water to 98% ethanol, a poorer ionising solvent, will greatly decrease the dissociation constant of cyanic acid, but will have a very much smaller effect on the dissociation constant of ammonium ions. The equilibrium $NH_4^+ + NCO^- \rightleftharpoons NH_3 + HNCO$ will therefore move to the right, and appreciable amounts of cyanic acid may be present. Unfortunately the dissociation constant of this acid in 98% ethanol is not known.

† The rate law for *carbonate* formation contains a kinetic term involving the hydrogen-ion concentration (see equation 3 of Part I).

[1] Walker and Appleyard, *J.*, 1896, **69**, 193.
[2] Miller and Nicholson, *Proc. Roy. Soc.*, 1938, **168**, *A*, 206.
[3] Wyatt and Kornberg, *Trans. Faraday Soc.*, 1952, **48**, 454.

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comparison of the k_1's for the various compounds. Errors in K_{1v} also influence the value of k_1' ([$NRR'H_2^+$] depends on this constant), but the effect is only small since nearly all the *alkylammonium* is in the acid form under our experimental conditions.

TABLE 1. *Specific rates (in sec.$^{-1}$ mole^{-1} l.) for the formation of carbamides in water at* 60·10°.

NRR'H	$10^{-9}/K_a$ *	n_β †	$10^3 k_1'$ ‡	$10^{-2}k_1$	k_1/k_1 (calc.) §
NH_3	0·182	0	1·250 ϕ	0·915	1·9
NBu^tH_2	3·76	0	0·140	2·12	1·5
NAm^tH_2	3·76	0	0·165 □	2·50	1·7
NPr^iH_2	3·76	1	0·618	9·37	6·5
$NEtH_2$	3·76	2	1·116	16·9	11·8
NAm^iH_2	3·76	2	1·12 □	17·0	11·9
$NMeH_2$	3·43	3	1·695	23·4	16·8
NEt_2H	8·93	4	1·052	37·8	19·0
NMe_2H	5·78	6	3·202	77·8	46·2

* The base strength; K_a is the thermodynamic dissociation constant of $NRR'H_2^+$. † The number of C–H bonds directly attached to the central nitrogen atom. ‡ At ionic strength 0·25. § k_1 (calc.) from equation 3. ϕ Part I. □ From Walker and Appleyard's data [1] (see p. 2545).

The two alternative rate coefficients, k_1' and k_1, are given in Table 1 for the compounds now investigated. It can be seen that the base strength of the amine is certainly not the principal factor controlling the rate. The values of k_1' follow no simple sequence, but k_1 seems to depend mainly on the number of C–H bonds attached to the nitrogen atom of the amine, n_β; within the limits of experimental error, amines having the same n_β also have the same k_1.

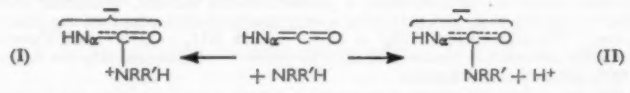
In Part I we assumed that urea and carbonate formation proceed by the addition of bases to cyanic acid. The appropriate rate coefficients for the four reactions involved are then predicted to within a factor of two by the Brönsted equation for base catalysis [4] in the form:

$$\log_{10}(k^\circ/q) = -1{\cdot}447 + 0{\cdot}3764 \log_{10}(p/qK_a) \quad . \quad . \quad . \quad . \quad (3)$$

where k° is the rate coefficient at zero ionic strength for reaction with a base of strength $1/K_a$, K_a is the thermodynamic dissociation constant of its conjugate acid, q the number of centres in the base which can accept a proton with equal ease, and p the number of equivalent, dissociable protons attached to different atoms in the conjugate acid. For the addition of amines to cyanic acid $k^\circ = k_1$, and the present values of k_1 are compared with those calculated from equation 3 in the last column of Table 1. It can be seen that this equation predicts the rates for *tert.*-amylamine and *tert.*-butylamine as well as can be expected, but the calculated values for the other amines are much too small; k_1/k_1 (calc.) increases with increasing n_β.

DISCUSSION

By analogy with the mechanism proposed in Part I for the formation of urea, the present reactions can be considered to involve nucleophilic addition of the amine to cyanic acid by one of the following two processes:



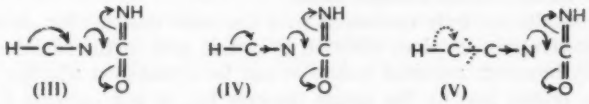
Rapid proton-transfer [prototropic change in (I) or proton addition to (II)] then yields

[4] Brönsted and Pedersen, *Z. phys. Chem.*, 1924, **108**, 185; Brönsted, *Chem. Rev.*, 1928, **5**, 332; Bell, "Acid–Base Catalysis," Clarendon Press, Oxford, 1941, p. 85.

the alkyl-urea, and k_1 therefore represents the specific rate of the slow reaction stage.* A detailed discussion of our results is given below, but it is worth noting now that we have been unable to visualise any other acceptable scheme which is consistent with the figures in Table 1 and with the observation that the kinetics of urea formation are accurately predicted by equation 1 over wide ranges of pH and concentration (Part I).

It has been suggested that the base strength of an amine may control its rate of reaction with cyanic acid, apart from complications caused by steric effects.[5] Our results do not confirm this view; the values of k_1 show no relation with the base strength (see Table 1), and an examination of scale-models with $\angle N_\alpha CO = 120°$, and calculations assuming $\angle N_\alpha CO = 180°$,[6] reveal no significant steric compressions in either (I) or (II). There are, however, considerable similarities with other reactions involving nucleophilic attack by amines. In ethereal solution, alkylamines with $n_\beta = 2$ react with phenyl *iso*cyanate at the same rate, and about ten times more rapidly than ammonia; [7] the corresponding factor in the present reactions is eighteen. The attack of amines on 1-chloro-2 : 4-dinitrobenzene follows the rate sequence dimethylamine > piperidine > methylamine,[8] but the base strength decreases in the order piperidine > dimethylamine > methylamine. Steric hindrance is not envisaged in these reactions,[8] and the rates decrease with decreasing n_β, as in the present systems.

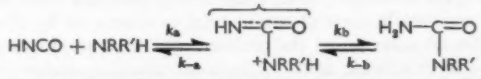
Passage into the transition state of amine addition to cyanic acid requires a displacement of the lone-pair electrons on the central nitrogen atom in the direction further away from the rest of the molecule, and thus results in a demand for electrons at the reaction centre. All the amines now considered have roughly the same base strength, steric effects have already been excluded, and it therefore seems reasonable to assume that the different reactivities arise from differences in the constitutional ability to stabilise the transition



(III) (IV) (V)

state by electron-release. Such a release of electrons is quite feasible in view of the polarisability of C–H bonds by the hyperconjugative mechanism † when linked to a suitably situated electron-demanding centre. Full hyperconjugation with the reaction centre (III) is considered unlikely as this would offend the principle of octet preservation,‡ but

* The validity of this statement can be readily demonstrated. The proposed reaction scheme is:



There is no evidence that the intermediate addition complex ever reaches detectable concentrations, and the stationary-state principle will therefore apply to this species. If we assume that the equilibrium between cyanic acid and cyanate ions is not upset by the reactions a comparison of the theoretical rate law with equation 2 shows that

$$k_1 = \frac{k_b k_a}{k_{-a}(1 + k_b/k_{-a})} \text{ and } k_2 = \frac{k_{-b}}{1 + k_b/k_{-a}}$$

Now k_{-b} refers to the transfer of a proton from one nitrogen atom to another and is therefore most unlikely to be less than 10^{-2} sec.$^{-1}$. Since $k_2 \sim 10^{-6}$, $k_b/k_{-a} > 10^4$ and hence $k_1 = k_a$ with negligible error. The same conclusion is obtained if the cyanic acid concentration is calculated from the stationary-state approximation.

† Ingold's nomenclature [9] is employed throughout this discussion.

‡ It has, however, been postulated that quinquevalent nitrogen may exist under some conditions.[10]

[5] Frost and Pearson, "Kinetics and Mechanism," Chapman and Hall, London, 1952, p. 263.
[6] Baker and Holdsworth, *J.*, 1947, 713.
[7] Davies and Ebersole, *J. Amer. Chem. Soc.*, 1934, **56**, 885.
[8] Brady and Cropper, *J.*, 1950, 507.
[9] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, ch. II.
[10] Gillespie, *J.*, 1952, 1002.

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it has been pointed out that hyperconjugation must also involve participation by the valence-bond structure corresponding to the simple ionisation of C–H.[11] A part of this type of electron-displacement can be relayed to an adjacent atom by the inductive mechanism. Thus, a C–H bond in (IV) can respond to electron-demand at the reaction centre and therefore stabilises the transition state, but the poor relay of inductive effects along saturated carbon–carbon systems makes the stabilising effect of such a bond in (V) extremely small, if not negligible. On this view, the number of C–H bonds attached to the central nitrogen atom of the amine should control its rate of reaction with cyanic acid, *i.e.*, k_1 should increase with increasing n_β, as observed. The similar observations in those reactions of amines with 1-chloro-2 : 4-dinitrobenzene which are not sterically hindered can be explained in the same manner.

tert.-Butylamine and *tert.*-amylamine react at rates which are predicted as well as can be expected by the Brönsted equation for base catalysis (equation 3). None of the groups in these two bases or the four which were employed in Part I to set up this equation (water, ammonia, hydroxide ions, and carbonate ions) is polarisable with respect to electron-demand at the reaction centre, and it is then reasonable to expect a linear relation between the free-energy of activation for addition to cyanic acid and the standard free-energy change for protonation, as observed. It has, however, been noted before (cf. ref. 12) that the Brönsted equation may not apply when polarisable groups are present—the electron displacements in the conjugate acid need not now parallel those in the transition state of another reaction—and the observation (Table I) that k_1/k_1 (calc.) increases with increasing n_β suggests that polarisable groups in an amine stabilise the transition state of the addition reaction more than they stabilise the corresponding alkylammonium ion. This conclusion is to be expected if this transition state is associated with the greater electron-demand at the central nitrogen atom.

The present results are fully consistent with the view that the formation of urea and its substituted derivatives involves addition to cyanic acid in the rate-determining step. Further work is, however, required before it can be established whether the activation process requires proton loss by the amine (process II), or not (process I). The former process would be retarded by electron-releasing substituents, but the observed accelerating effect of such groups merely indicates that the formation of the N–C bond is more important than the fission of the N–H bond.

Experimental

Materials and Rate Measurements.—Alkylammonium chlorides were obtained in a sufficient state of purity by the recrystallisation of commercial products, or by the action of dry hydrogen chloride on the ethereal solution of the amines; the final products never contained more than 0·3% of amine or hydrochloric acid. Alkylammonium cyanates were prepared in 0·5M-solution by shaking the chlorides with a slight excess of silver cyanate; for details, see Part I.

NN-Dimethylurea was prepared by treating pure sodium cyanate with dimethylammonium chloride in water, removing the solvent under reduced pressure, and recrystallising the product from methanol. *NN*-Diethylurea was obtained by analogous methods and recrystallised from ether.

Acetone was purified by Conant and Kirner's method,[13] and all distilled water used in the experiments was passed through a mixed-resin exchange column and equilibrated with respect to atmospheric carbon dioxide.

Rates were measured at 60·10° (±0·02°) by the sealed-tube technique. Reaction mixtures were made up by volume at 0° to contain *ca.* 0·05M-cyanate, 0·002—0·004M-sodium hydroxide, and sufficient potassium nitrate to bring the initial ionic strength to 0·25 at the reaction temperature. All the cyanates were studied at two or more different sodium hydroxide concentrations. The reactions were followed by determining the total basicity,

[11] Hine, "Physical Organic Chemistry," McGraw-Hill, New York, 1956, p. 22.
[12] de la Mare and Vernon, *J.*, 1956, 41.
[13] Conant and Kirner, *J. Amer. Chem. Soc.*, 1924, **46**, 245.

$X = Cy + 2C + [OH^-]_i$ (g.-equiv. l.$^{-1}$), and the basicity after all the cyanate had been removed, $Y = 2C + [OH^-]_i$, where Cy and C are the *cyanate* and *carbonate* * concentrations, respectively, and $[OH^-]_i$ represents the concentration of the added hydroxide ions before any reaction with the acids present. For details, see Part I.

Calculations.—The stoicheiometric equations (i), (ii),† and (ii*a*) show that at any stage of the reaction

$$\left.\begin{aligned} N_o - N = U - U_o &= (Cy)_o - Cy + C_o - C + U_o' - U' \\ \text{and} \qquad N' - N_o' &= C - C_o + U_o' - U' \end{aligned}\right\} \quad . \quad . \quad . \quad (4)$$

where N, N', U, and U' are the concentrations of alkylammonium, ammonium, substituted urea, and urea, respectively, and the subscript o refers to " zero time " (*i.e.*, the time of the first reading which was usually taken two or three minutes after immersion in the thermostat). N_o and U_o were obtained by analysing the reaction mixture before its introduction in the thermostat, and assuming that no reaction had taken place at this stage.

Our analytical procedure allows calculation of all the stoicheiometric concentrations provided $U' - U_o'$ is known. Unfortunately accurate determination of small amounts of urea in the presence of a considerable excess of its substituted derivatives is difficult, but urea formation is slow under the existing experimental conditions,‡ and the term $U' - U_o'$ in equation (4) was therefore neglected in our calculations. In most cases this procedure has a negligibly small effect on the rate coefficients for the formation of the substituted ureas. The data in Table 2 show that in the decomposition of diethylammonium cyanate the urea concentration is always less than 0·3% of the diethylurea concentration, and even this figure represents an overestimate since it was obtained by assuming that $N' - N_o' = C - C_o$ at all stages of the reaction; the corresponding figures for methyl-, ethyl-, and dimethyl-ammonium cyanate are lower still. In the slower decompositions of *iso*propyl- and *tert.*-butyl-ammonium cyanate, however, urea formation makes a greater contribution to the overall reaction and its neglect leads to rate coefficients (for the formation of the substituted ureas) which are initially constant but decrease as the reaction proceeds. This effect is more pronounced for the *tert.*-butyl compound which reacts more slowly under our experimental conditions than any of the other compounds investigated. Rate coefficients for these two systems were obtained by extrapolation to " zero time."

The actual concentrations of the various species present in a reaction mixture can be obtained from the analytical results and the appropriate dissociation constants, provided the concentration of the hydroxide ions is known. Using methods analogous to those already described in Part I, and omitting terms which are negligible under the present experimental conditions, we have

$$[OH^-]_i - [OH^-] = \frac{[OH^-]}{[OH^-] + K_{iv}} \cdot N - \frac{K_v}{[OH^-] + K_v} \cdot C + \frac{[OH^-]}{[OH^-] + K_{iv}'} \cdot N' \qquad (5)$$

where $K_{iv} = [NRR'H_2^+][OH^-]/[NRR'H]$, $K_{iv}' = [NH_4^+][OH^-]/[NH_3]$, and $K_v = [HCO_3^-][OH^-]/[CO_3^{2-}]$. This equation can be solved graphically by assuming that $N' = C$. Under our experimental conditions, however, the last two terms then only make a very small contribution. If they are neglected, the resulting quadratic equation readily yields $[OH^-] = [OH^-]_i K_{iv}/(N + K_{iv} - [OH^-]_i)$, since $(N + K_{iv} - [OH^-]_i)^2 \gg [OH^-]_i K_{iv}$, and hence $[NRR'H_2^+] = N\{1 - [OH^-]_i/(N + K)\}$. Errors resulting from this procedure increase as the reaction proceeds, but they are usually too small to have any significant effect on the integrated rate coefficients. For example, the data in Table 2 lead to the conclusion that $[NRR'H_2^+]$ calculated directly from equation (5) is only 1% greater at 45% reaction than the value obtained by the approximate method, and only 2% greater at 60% reaction. Larger errors are to be expected in the slower reactions (*iso*propyl and *tert.*-butyl compounds) where $N' < C$ since significant urea formation now occurs. This accounts for the decreasing rate

* See footnote, p. 2544.

† It is necessary to consider reaction (ii) since *carbonate* formation by reaction (i) also produces ammonium.

‡ In alkaline solution only a small fraction of the *ammonium* is present as ammonium ions ($dU'/dt = k_1'[NCO^-][NH_4^+]$), and the *ammonium* concentration does not reach large values since $dN'/dt \leqslant dC/dt = k_3'[NCO^-] + k_4'[H_3O^+][NCO^-] + k_5'[HCO_3^-][NCO^-]$ (Part I, equation 3).

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coefficients observed in these systems since $[OH^-]$ calculated by the approximate method is now too small, resulting in too large a value for $[NRR'H_2^+]$.*

Values for K_{1v} and K_{1v}' at 60° and ionic strength 0·25 were obtained from the thermodynamic dissociation constants of the conjugate acids,[14] the ionic product of water,[15] and the ionic activity coefficients given by Davies's equation; [16] the values are given below. Accurate data for the amines containing branched alkyl groups were not available at our reaction temperature and it was therefore assumed that K_{1v} had the same value as for ethylamine. This may represent a slight overestimate,[17] but errors in this direction do not affect the conclusions regarding the variation of k_1 with amine structure. The values for K_{iii} (see p. 2545) and K_v were the same as in Part I.

NRR'H	NH_3	$NMeH_2$	$NEtH_2$	NMe_2H	NEt_2H
10^4K_{1v}	0·352	6·63	7·28	11·2	17·3

$10^{16}K_{iii} = 4·81$, $10^4K_v = 6·41$

Reaction Rates.—The rate coefficients k_1' were obtained from the integrated form of equation (1):

$$k_1' = \frac{U - U_0 + k_2\int_0^t U\,.\,dt}{\int_0^t [NRR'H_2^+][NCO^-]\,.\,dt}$$

The integrals were evaluated graphically. Neglect of the term in k_2 gave constant values of k_1' for methyl- and ethyl-ammonium cyanate and it was therefore assumed that here the decomposition of the substituted urea was too slow to affect the observed rate. For dimethyl and diethyl compounds, however, the neglect of this term led to decreasing values of k_1', but these became constant when this term was included; k_2 was determined from measurements on the substituted urea by the methods already described in Part I. Rate coefficients k_1 were obtained from the corresponding k_1' and the appropriate equilibrium constants.

TABLE 2. *Illustrating the decomposition of ethylammonium cyanate.*

Temp. = 60·10°; initial ionic strength = 0·25; $[OH^-]_i = 0·00384$; $10^4U_0 = 2·5$; $C_0 = 0$. t in sec., k_1' in sec.$^{-1}$ mole^{-1} l.

		10^4C				
$10^{-3}t$	10^2Cy	obs.*	calc.†	$10^3(U - U_0)$	$10^3U'$ ‡	$10^3k_1'$
0	$4·46_5$	—	—	—	—	—
13·80	$4·20_8$	0·6	0·7	$0·25_1$	0·03	$1·06_6$
18·00	$4·11_3$	0·7	0·8	$0·34_5$	0·06	$(1·14_2)$
34·20	$3·86_5$	1·5	1·5	$0·58_5$	0·2	$1·09_7$
63·60	$3·49_9$	2·7	2·8	$0·93_9$	0·6	$1·05_9$
82·20	$3·29_0$	3·5	3·5	$1·14_0$	1·0	$1·06_2$
109·2	$3·05_2$	4·6	4·5	$1·36_6$	1·5	$1·04_7$
153·6	$2·68_3$	6·1	6·0	$1·72_2$	2·6	$1·07_3$
180·6	$2·52_0$	6·8	6·7	$1·87_7$	3·2	$1·07_3$
208·2	$2·39_1$	7·7	7·6	$1·99_7$	3·9	$1·06_3$
238·8	$2·25_1$	8·7	8·5	$2·12_6$	4·6	$1·06_2$
277·2	$2·11_1$	9·7	9·6	$2·25_7$	5·5	$1·05_8$
327·0	$1·95_2$	11·0	10·9	$2·40_3$	6·7	$1·05_8$
358·2	$1·87_1$	11·6	11·7	$2·47_8$	7·4	$1·05_6$

$10^3k_1'$ (mean) = 1·064, a duplicate run ($[OH^-]_i = 0·00192$) gave 1·039.

* From the smoothed curve, C against t. † Part I, equation (3). ‡ Calculated from equation (1) by assuming $N' = C$.

Details of a typical run are given in Table 2 where it is also shown that *carbonate* formation follows the rate law proposed in Part I.

* The decomposition of the substituted urea, which was not investigated for these systems, may also contribute to the decreasing rate coefficients.

[14] Everett and Wynne-Jones, *Proc. Roy. Soc.*, 1941, **177**, *A*, 499; Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 34.

[15] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, equation 15–3–6a.

[16] Davies, *J.*, 1938, 2093.

[17] Personal communication from Dr. H. K. Hall, jun.

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Errors in k_1 and k_1' resulting from the use of the Davies equation [16] in calculating the ionic activity coefficients have already been discussed in Part I. Any such errors will, however, have a negligible effect on the present comparison of the reactivities of a series of amines.

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517. *A Detailed Refinement of the Crystal and Molecular Structure of Thiourea.*

By N. R. KUNCHUR and MARY R. TRUTER.

A three-dimensional *X*-ray crystal-structure analysis of thiourea has been made. The anisotropic thermal motion has been analysed and the bond lengths corrected for systematic errors arising from rotational oscillations of the molecule. The sulphur, carbon, and nitrogen atoms in each molecule are coplanar, with bond lengths C–N = 1·33 ± 0·01 Å and C–S = 1·71 ± 0·01 Å, and angles S–C–N = 122·2° ± 0·6° and N–C–N = 115·6° ± 1·1°.

THIOUREA is conventionally written $S{=}C(NH_2)_2$ but its reactions show that the zwitterion $^-S{-}C(=NH_2^+)NH_2$ must also be considered. The Raman spectrum [1] of the solid has been interpreted as indicating that the ionic form is predominant; on the other hand the approximate bond lengths,[2] C–S = 1·64 and C–N = 1·35 ± 0·1 Å, are confusing because both seem to show a good deal of double-bond character. A refinement of the *X*-ray analysis of this simple molecule has therefore been undertaken in order to provide more accurate bond lengths for comparison with theory and also with the bond lengths in co-ordination compounds containing thiourea.[3]

Wyckoff and Corey [2] found that there were four molecules in the orthorhombic unit cell (a = 7·68, b = 8·57, c = 5·50 Å) with space group $Pnma$–D_{2h}^{16}. (For convenience Wyckoff and Corey's b and c axes have been interchanged to conform with the space-group orientation in the International Tables.[4]) In each molecule the carbon and the sulphur atom lie on a mirror plane with the two equivalent nitrogen atoms on either side of it. The co-ordinates determined by two-dimensional analysis were C, 0·10, ¼, −0·14; S, −0·007, ¼, 0·12; N, 0·13, 0·125, $-0{\cdot}27_8$. The molecule was planar within the limits of experimental error.

Isotropic Refinement by Three-dimensional Methods.—The intensities of the 260 reflections observable with copper radiation were measured; few spots of high values of sin θ were observed so that very little additional information could have been obtained by the use of radiation of shorter wavelength at room temperature. Preliminary calculation showed good agreement between the observed structure amplitudes, $|F_{obs}|$, and those calculated from Wyckoff and Corey's co-ordinates which were therefore taken as a starting point for three-dimensional analysis. The atomic scattering factors used were those given by McWeeny [5] for carbon and nitrogen and by James and Brindley for sulphur,[6] multiplied by a temperature factor $\exp(-B\sin^2\theta/\lambda^2)$. This theoretical scattering factor for sulphur was chosen in preference to empirical values [7] determined more recently because the latter are not independent of the anisotropic thermal motion and bonding in the structures from which they were derived.

The co-ordinates were refined in three successive stages by calculation of differential syntheses [8] with a back-shift correction for finite-series effects, and at each stage the

[1] Kohlrausch and Wagner, *Z. phys. Chem.*, 1940, *B*, **45**, 229.
[2] Wyckoff and Corey, *Z. Krist.*, 1932, **81**, 386.
[3] Truter, *Acta Cryst.*, 1957, **10**, 785.
[4] "International Tables for *X*-ray Crystallography," 1952, Kynoch Press, London.
[5] McWeeny, *Acta Cryst.*, 1951, **4**, 51.
[6] "International Tables for the Determination of Crystal Structures," Borntraeger, Berlin, 1935.
[7] Cox, Gillot, and Jeffrey, *Acta Cryst.*, 1949, **2**, 356; Abrahams, *ibid.*, 1955, **8**, 661.
[8] Booth, *Trans. Faraday Soc.*, 1946, **42**, 444.

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scale and temperature factors were altered to make the observed and calculated mean curvatures and peak values of the electron-density distributions more nearly equal. (Because of the uncertainty in their structure amplitudes, planes which gave reflections too weak to be observed were omitted from the refinement.) These refinement operations and their results are summarised below {R is the agreement index, $\sum(|F_{obs}| - |F_{calc}|)|/\sum|F_{obs}|$}. The smallness of the co-ordinate shifts in the last cycle showed that no further improvement was possible by isotropic refinement, even though (as the figures below show) the mean B factor for carbon had not yet been adjusted to its best value. However, the need for anisotropic adjustment of the parameters was shown by the variation with direction of the observed curvature of the electron density in each atom; in the Table below r_x, r_y, and r_z are respectively the ratios of the observed curvatures, $\partial^2\rho/\partial x^2$, $\partial^2\rho/\partial y^2$, and $\partial^2\rho/\partial z^2$, to the corresponding calculated curvatures; ρ is the peak electron density:

Cycle	B (Å^2) sulphur	B (Å^2) nitrogen	B (Å^2) carbon	R	Max. co-ordinate shift (Å)
1	4·0	4·0	4·0	0·20	0·18
2	3·5	4·5	4·5	$0{\cdot}16_3$	0·04
3	3·5	4·5	4·24	$0{\cdot}15_8$	0·01

	ρ_{obs}/ρ_{calc}	r_x	r_y	r_z
C	1·01	1·06	1·10	1·14
S	0·98	0·92	0·99	1·09
N	0·94	0·85	1·03	1·01

It can be seen that for all atoms r_x is smaller than the other two ratios, which indicates that the thermal motion is greatest in the direction of the a axis, *i.e.*, the axis which is most nearly normal to the planes of the molecules.

Determination of the Anisotropic Thermal Parameters.—A method of successive refinement for determining anisotropic thermal-motion parameters has been described by Cruickshank,[9] who also gives the refinement equations.

After three cycles of anisotropic refinement the agreement index was reduced to 0·112, the following parameters, which resulted from the third cycle, being used to calculate the structure factors:

	x/a	y/b	z/c	b_{33} ($\times 10^5$)	b_{23} ($\times 10^5$)	b_{22} ($\times 10^5$)	b_{13} ($\times 10^5$)	b_{12} ($\times 10^5$)	b_{11} ($\times 10^5$)
C	0·09151	0·25000	$\bar{0}{\cdot}\bar{1}\bar{6}\bar{2}\bar{7}\bar{8}$	1161	0	1331	2115	0	1140
S	$\bar{0}{\cdot}\bar{0}\bar{0}\bar{7}\bar{2}\bar{6}$	0·25000	0·11400	1770	0	1069	266	0	1789
N	0·13160	0·12011	0·27742	3885	819	1011	3026	$\bar{1}\bar{7}\bar{3}$	2941

The figures given are those actually used, although, as shown below, they are not all significant. The parameters b_{ij} for each atom were used in the expression $\exp(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)$ to give the temperature factor for each hkl. A list of observed and calculated structure factors is given in Table 1; the scale factor, obtained by the criterion given above, also made $\sum|F_{obs}|$ equal to $\sum|F_{calc}|$ where the summations are over all planes allowing for multiplicity. The poor agreement for the planes (020), (200), and (101) may be due to extinction; if these planes are omitted the scale factor is altered by 0·3% and the agreement index R is reduced to 0·109.

A fourth differential synthesis was carried out and the maximum change required in the atomic co-ordinates was 0·005 Å (in x_N). The final co-ordinates and their standard deviations (calculated from Cruickshank's formula [10]) are:

	x/a	y/b	z/c	x (Å)	$\sigma(x)$ (10^3 Å)	y (Å)	$\sigma(y)$ (10^3 Å)	z (Å)	$\sigma(z)$ (10^3 Å)
C	0·0916	0·2500	$\bar{0}{\cdot}\bar{1}\bar{6}\bar{3}\bar{2}$	0·701	8	2·134	0	$\bar{0}{\cdot}\bar{9}\bar{0}\bar{1}$	13
S	$\bar{0}{\cdot}\bar{0}\bar{0}\bar{7}\bar{3}$	0·2500	0·1138	$\bar{0}{\cdot}\bar{0}\bar{5}\bar{6}$	2	2·134	0	0·628	2
N	0·1322	0·1201	$\bar{0}{\cdot}\bar{2}\bar{7}\bar{6}\bar{7}$	1·012	11	1·025	10	$\bar{1}{\cdot}\bar{5}\bar{2}\bar{7}$	11

The standard deviation of the electron density is 0·2e/Å^3.

[9] Cruickshank, *Acta Cryst.*, 1956, **9**, 747.
[10] *Idem*, *ibid.*, 1949, **2**, 65.

TABLE 1.

hkl	F (calc.)	F (obs.)	hkl	F (calc.)	F (obs.)	hkl	F (calc.)	F (obs.)	hkl	F (calc.)	F (obs.)	hkl	F (calc.)	F (obs.)	hkl	F (calc.)	F (obs.)
000	(160)	—	111	—	—	113	—	—	125	13	14	102	2	3	273	10	14
020	−66	44	121	−40	37	123	24	24	135	—	—	112	−34	41	283	—	—
040	17	17	131	5	7	133	−7	7	145	−9	10	122	−9	7	293	−7	7
060	−31	27	141	31	30	143	−22	24				132	19	17			
080	28	20	151	—	—	153	—	—	305	−10	12	142	9	10	403	6	7
0, 10, 0	−9	7	161	−18	17	163	11	14	315	—	—	152	−17	17	413	−13	14
			171	—	—	173	—	—	325	12	12	162	—	—	423	—	—
200	51	43	181	11	10	183	−6	7	335	—	—	172	16	15	433	21	20
210	−38	37	191	—	—				345	−11	14	182	—	—	443	—	—
220	−46	42	1, 10, 1	−7	7	303	−16	17				192	−8	10	453	−16	17
230	−14	20				313	—	—	505	−8	7						
240	35	37	301	26	27	323	11	10	515	—	—	302	6	7	603	6	10
250	—	—	311	—	—	333	−9	10	525	10	7	312	−29	30	613	−11	14
260	−22	20	321	−22	25	343	−8	10	535	—	—	322	−12	10	623	—	—
270	10	10	331	4	7	353	5	7	545	−10	10	332	28	27	633	7	7
280	14	10	341	16	18	363	8	10				342	12	14			
290	−4	3	351	—	—				011	14	14	352	−20	20	104	—	—
2, 10, 0	−9	7	361	−13	14	503	−8	10	031	39	38	362	—	—	114	−8	7
			371	—	—				051	−23	20	372	12	14	124	—	—
400	—	—	381	9	10	004	−19	17				382	—	—	134	13	10
410	—	—	501	15	14	024	26	27	201	50	47	392	−9	8	144	—	—
420	−21	20	511	—	—	044	−28	27	211	−23	25				154	−9	9
430	—	—	521	−11	10	064	15	14	221	−11	7	502	6	7			
440	29	27	531	—	—	084	−7	7	231	16	18	512	−21	20	304	—	—
450	—	—	541	8	8				241	−12	12	522	—	—	314	—	—
460	−11	10	551	—	—	204	−24	20	251	−13	11	532	23	20	324	—	—
470	—	—	561	−7	8	214	—	—	261	−7	7	542	—	—	334	—	—
480	4	3				224	21	20	271	10	9	552	−17	15	344	−7	8
490	—	—	701	7	7	234	—	—	281	10	10	562	—	—			
4, 10, 0	−6	3	711	4	5	244	−15	15	291	−6	7	572	10	10	015	7	7
			721	−7	8	254	—	—									
600	13	10	731	—	—	264	13	7	401	6	8	702	—	—	106	—	—
610	10	10	741	6	6				411	−33	30	712	−12	10	116	10	11
620	−10	10				404	−18	17	421	−9	10	722	—	—	126	—	—
630	—	—	002	−33	30	414	—	—	431	9	10	732	10	10	136	−12	10
640	7	7	022	−1	7	424	12	14	441	8	10				146	—	—
650	—	—	042	18	17	434	—	—	451	−9	10	013	−37	41	156	9	7
660	−7	7				444	−7	7	461	−4	3	033	12	14			
670	−5	3	202	5	7	454	—	—	471	14	14	053	−11	14	306	—	—
680	5	3	212	21	24	464	8	3				073	16	17	316	13	13
			222	—	—				601	−4	3	093	−9	8			
800	10	7	232	10	10	604	−6	7	611	−13	14				506	—	—
810	6	3	242	—	—	614	—	—	621	—	—	203	−11	14	516	9	8
820	−7	7	252	—	—	624	—	—	631	14	15	213	−22	25			
830	−6	7	262	—	—	634	—	—	641	7	7	223	—	—			
840	—	—	272	−9	9	644	−8	8	651	−10	8	233	22	20			
850	5	3	402	17	17				661	—	—	243	12	14			
						105	−20	17	671	—	—	253	−17	17			
101	41	34	103	−18	17	115	—	—	681	−2	3	263	—	—			

The peak value of the electron density for each atom is given below together with the ratios of the observed and calculated values of the electron densities and curvatures.

	ρ_{obs} (e/Å^3)	ρ_{obs}/ρ_{calc}	r_x	r_y	r_z
C	7·0	0·95	1·00	1·00	0·97
S	28·0	1·00	1·00	0·99	1·02
N	7·2	1·01	1·00	0·99	0·98

The ratios still differ slightly from unity, and the final thermal parameters (all $\times 10^3$) quoted below have been obtained by calculating the changes corresponding to the differences between the observed and calculated curvatures.

	b_{33}	b_{22}	b_{23}	b_{13}	b_{12}	b_{11}	$\sigma(b_{33})$	$\sigma(b_{22})$	$\sigma(b_{11})$
C	14	0	13	28	0	11	8	2	3
S	18	0	11	3	0	18	2	0·4	0·6
N	40	8	10	32	$\bar{1}$	29	8	2	3

The standard deviations, $\sigma(b_{ii})$, are derived from the expression:

$$\sigma^2(b_{ii}) = \{\tfrac{8}{5}\sum h_i^4\,\sigma^2(F)\}/(\sum h_i^4 f)^2$$

given by Cruickshank,[9] in which f is the scattering factor and $\sigma^2(F)$ is taken as $(|F_{obs}| - |F_{calc}|)^2$.

Analysis of the Anisotropic Thermal Motion.—Cox, Cruickshank, and Smith [11] have

[11] Cox, Cruickshank, and Smith, *Nature*, 1955, **175**, 766.

shown that rotational oscillations of molecules can give rise to systematic errors in bond lengths determined by *X*-ray methods, so that an analysis of the thermal motion of the molecule is necessary before the final corrected bond lengths can be given.

The mean square amplitudes of vibration of an atom in any direction can be represented by the radius of an ellipsoid; the magnitudes and orientation of the axes of this ellipsoid can be calculated from the six numbers b_{ij}. In the direction of the unit cell edge of length a_i the mean square amplitude of vibration, μ_{ii}^2, is given by $\mu_{ii}^2 = b_{ii}a_i^2/2\pi^2$. The cross terms, μ_{ij}^2 ($\mu_{ij}^2 = b_{ij}a_ia_j/4\pi^2$, where $i \neq j$), are required with the three values of μ_{ii}^2 to determine the dimensions and orientation of the ellipsoid; only if the values of b_{ij} are zero will the axes of the ellipsoid be parallel to the crystallographic axes. From the six values of μ^2 for all atoms we can derive (*a*) the r.m.s. amplitudes and directions of maximum and minimum thermal vibration of each atom with respect to the crystallographic axes, (*b*) the same quantities with respect to a set of molecular axes, and (*c*) the r.m.s. amplitudes of angular oscillation and translational vibration of the molecule as a whole assuming it to be a rigid body.

(*a*) The maximum and minimum r.m.s. amplitudes of vibration, $\mu_{max.}$ and $\mu_{min.}$, derived from the lengths of the major and minor axes of the ellipsoids, and their direction cosines are given in Table 2 with, for comparison, the direction cosines of the normal to the molecular plane and of the bonds.

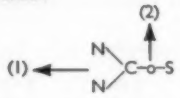
TABLE 2.

	μ_{max} (Å)	Direction	μ_{min} (Å)	Direction
C	0·232	(0·785, 0, 0·620)	0·040	(0·620, 0, $\bar{0}$·$\bar{7}\bar{8}\bar{5}$)
S	0·231	(0·992, 0, 0·129)	0·163	(0·129, 0, $\bar{0}$·$\bar{9}\bar{9}\bar{2}$)
N	0·333	(0·812, ±0·057, 0·581)	0·169	(0·383, ±0·699, $\bar{0}$·$\bar{6}\bar{0}\bar{4}$)
	Normal	(0·896, 0, 0·444)	C–S	(0·444, 0, $\bar{0}$·$\bar{8}\bar{9}\bar{6}$)
			C–N	(0·237, 0·846, $\bar{0}$·$\bar{4}\bar{7}\bar{8}$)
			C–N′	(0·237, $\bar{0}$·$\bar{8}\bar{4}\bar{6}$, $\bar{0}$·$\bar{4}\bar{7}\bar{8}$)

The angles between the various directions are

between μ_{max}(C) and normal, 12°
between μ_{max}(S) and normal, 19°
between μ_{max}(N) and normal, 10°
between μ_{min}(S) and C–S bond, 19°
between μ_{min}(N) and C–N bond, 14°

(*b*) Molecular axes were chosen thus:



with axis (3) as the normal to the molecular plane through the mass centre, o. Tensor transformations (Cruickshank [12]) gave the following mean square amplitudes U_{ij} (all in Å^2) referred to these axes:

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
C	0·004	0	$\bar{0}$·$\bar{0}\bar{1}\bar{3}$	0·049	0	0·051
S	0·030	0	0·008	0·041	0	0·051
N	0·039	$\bar{0}$·$\bar{0}\bar{1}\bar{0}$	$\bar{0}$·$\bar{0}\bar{1}\bar{4}$	0·038	0·003	0·109
N′	0·039	0·010	$\bar{0}$·$\bar{0}\bar{1}\bar{4}$	0·038	$\bar{0}$·$\bar{0}\bar{0}\bar{3}$	0·109

From these we obtain the following r.m.s. amplitudes (in Å) of vibration:

along the normal, C, 0·227; S, 0·225; N, 0·330
along the C–S bond, C, 0·061; S, 0·172
along the C–N bond, C, 0·190; N, 0·173
perpendicular to the C–S bond in the molecular plane, C, 0·221; S, 0·202
perpendicular to the C–N bond in the molecular plane, C, 0·129: N, 0·211

[12] Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

(*c*) For the molecule as a whole the tensors T (in Å^2) and ω (in radians^2) for the mean square amplitudes of the translational and rotational motions can be obtained by suitable transformations.[12] The values are:

T_{11}	T_{12}	T_{13}	T_{22}	T_{23}	T_{33}
0·0234	0	0·0098	0·0332	0	0·0515
ω_{11}	ω_{12}	ω_{13}	ω_{22}	ω_{23}	ω_{33}
0·0470	0	0·0020	0·000	0	0·0077

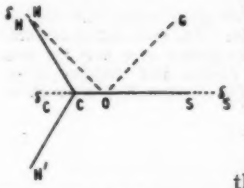
giving a r.m.s. angular oscillation of 5·0° about axis (3), 0° about (2), and 12·5° about (1), *i.e.*, the main oscillation is about an axis through the C–S bond. The r.m.s. amplitudes of translation are 0·153 Å along axis (1), 0·182 Å along (2), and 0·227 Å along (3).

The effect of rotational oscillation is to make an atom, P, appear closer to the centre of oscillation, O (taken as the mass centre), by a small distance δ which can be determined from the relation:[13]

$$\delta = \frac{1}{2r}\left\{\frac{s^2}{1 + s^2/q^2} + \frac{t^2}{1 + t^2/q^2}\right\}$$

where r is the uncorrected distance from O to P, $q^2 = \rho/(\delta^2\rho/\delta x_{ii}^2)$, and s^2 and t^2 are the mean square amplitudes of oscillation about two axes through O orthogonal to OP.

For carbon and sulphur $t^2 = \omega_{22}r^2$ and $s^2 = \omega_{33}r^2$, whence $\delta_O = 0{\cdot}0016$ Å and $\delta_S = 0{\cdot}0045$ Å and the correction to the C–S bond length is +0·006 Å. For nitrogen $s^2 = \omega_{33}r^2$ and $t^2 = r^2\omega_{OG}$, where OG is perpendicular to ON in the plane of the molecule. ω_{OG}, calculated from ω_{11}, ω_{12}, ω_{22}, and the direction cosines of OG, has the value 0·0231 radians^2, whence $\delta_N = 0{\cdot}0189$ Å. The correction to the C–N bond is the component of δ_N along the bond minus the component of δ_O along the bond and is 0·018 Å.



Hydrogen Atoms.—When the anisotropic thermal motion for the other atoms had been determined, attempts were made to locate the hydrogen atoms. First the intermolecular N–S distances were calculated; the shortest N–S distance (see Figure) is 3·42 Å which, being longer than the sum of the van der Waals radii (3·35 Å), indicates that there is no hydrogen bonding, so that no deductions could be made in this way about the positions of the hydrogen atoms.

By analogy with urea[14] the hydrogen atoms would be expected to lie in the plane of the heavy atoms forming, with the carbon atom, a trigonal arrangement about the nitrogen atom; these positions have been designated H_1 and H_2. Another position consistent with trigonally hybridised nitrogen would be with the H–N–H plane perpendicular to the S–C–N–N′ plane; these positions are designated H_3 and H_4. However, three-dimensional values for $\rho_{obs} - \rho_{calc}$ at all four postulated hydrogen positions did not differ significantly from the standard deviation in the electron density (0·2e/Å^3) and calculation of structure factors with hydrogen atoms at either H_1 and H_2 or H_3 and H_4 with an isotropic $B = 5{\cdot}0$ Å^2 gave no change in the agreement index.

Hydrogen atoms in any position should be shown by a $\rho_{obs} - \rho_{calc}$ projection, the most favourable one being along the [010] axis on to the mirror plane. This projection was calculated and is shown in the Figure where the positions of the heavy atoms and the previously postulated hydrogen atoms are marked. In fact the only appreciable electron density, 1·7e/Å^2, is at $x/a = 0{\cdot}183$, $z/c = 0{\cdot}400$ and a line difference synthesis along y through this point showed peaks of 0·4 and 0·5e/Å^3 at $y/b = 3/4$ and 1/4 respectively, and some additional peaks of 0·2e/Å^3. The individual peaks are not of significant height and are 2 Å from the nearest atom (S).

These results suggest that the thermal motion of the hydrogen atoms is so large that

[13] Cruickshank, *Acta Cryst.*, 1956, **9**, 757.
[14] Worsham, Levy, and Peterson, *ibid.*, 1957, **10**, 319; Vaughan and Donohue, *ibid.*, 1952, **5**, 530.

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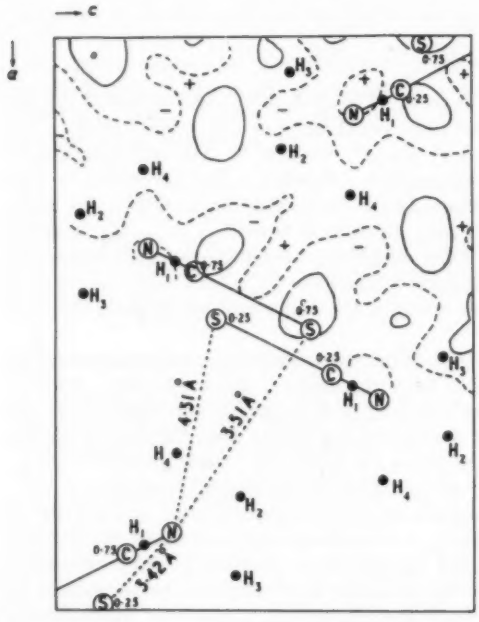
the peak electron density has been reduced to an insignificant level; completely free rotation, however, is not consistent with some preliminary nuclear magnetic resonance observations.[15]

Dimensions of the Molecule.—For comparison the bond lengths and angles and their standard deviations are given below after (*a*) isotropic refinement, (*b*) anisotropic refinement, and (*c*) correction for rotational oscillation:

	C–S (Å)	σ (Å)	C–N (Å)	σ (Å)	S–Ĉ–N	σ	N–Ĉ–N	σ
(*a*)	1·710	0·016	1·319	0·015	123·0°	0·8°	114·0°	1·6°
(*b*)	1·707	0·012	1·311	0·012	122·2	0·6	115·6	1·1
(*c*)	1·713	0·012	1·329	0·012	122·2	0·6	115·6	1·1

The molecule is accurately planar, the deviation from the plane being less than 0·0003 Å for all atoms other than hydrogen. The values of σ are derived from the estimated



Difference projection along [010] *with contour intervals of* 1 e/Å³. *The zero contour is dotted and contours are drawn over half the area only. For the carbon and sulphur atoms* y/b *is given. The shortest* N–S *separations are indicated.*

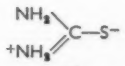
standard deviations in the atomic co-ordinates and do not allow for possible uncertainties in the corrections for rotational oscillation. Final values for the bond lengths are S–C = 1·71 ± 0·01 Å and C–N = 1·33 ± 0·01 Å, and for the angles S–C–N = 122·2° ± 0·6° and N–C–N = 116° ± 1°.

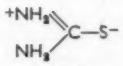
Discussion

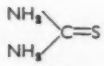
The carbon–sulphur (1·71 Å) and carbon–nitrogen (1·33 Å) bond lengths are significantly shorter than the generally accepted single-bond values, 1·82 and 1·475 Å, respectively. The double-bond lengths are not known accurately. For the carbon–nitrogen bond in *s*-triazine the order of which is at least 1·50, Lancaster and Stoicheff [16] obtained a very accurate value of 1·338 ± 0·001 Å, which is the same, within the limits of error, as in thiourea. This suggests that structures (I) and (II) must make a large contribution to the bonding, but the short carbon–sulphur bond with a bond order greater than 1·0

[15] Emsley and Smith, *Proc. Chem. Soc.*, 1958, 53.
[16] Lancaster and Stoicheff, *Canad. J. Physics*, 1956, **34**, 1016.

shows that there is also a contribution from the conventional form (III). Thus the apparent bonding capacity of the carbon atom is more than 4·0, a result which has been obtained for other π-bonded molecules and which indicates the need for a molecular-orbital treatment.


(I)


(II)


(III)

Davies and Hopkins [17] have recently carried out molecular-orbital calculations on urea, all the atoms of which, hydrogen included, have been shown experimentally [14] to be coplanar. They obtain the following results: (i) complete delocalisation of the two lone pairs of electrons on the nitrogen atoms being assumed, the bond order of both C–O and C–N is 1·50, and the agreement between the calculated delocalisation of resonance energy and Pauling's [18] empirical value is good; (ii) delocalisation of the lone pairs being assumed to be sufficient only to make the C–O bond order 1·60, which is the value found from force constants, the bond order calculated for C–N is 1·40 and the calculated resonance energy is smaller than Pauling's empirical value.

Since the carbon–nitrogen bond length in thiourea does not differ significantly from that in urea (1·35 Å) we may infer that the lone-pair electrons are delocalised to about the same extent in the two substances, but a detailed theoretical treatment of sulphur compounds is much more difficult than that of the corresponding oxygen compounds. Accordingly, and because few suitable data for comparison are available, further discussion will be deferred to a later paper in which accurate bond lengths for thioacetamide will be presented.

Experimental

Crystals of thiourea were grown from alcohol. The unit cell dimensions, determined by Straumanis's method from the reflections (501), (404), and (0, 10, 0), were found to be $a = 7{\cdot}655$, $b = 8{\cdot}537$, $c = 5{\cdot}520$ Å all $\pm$ 0·007 Å ($v = 360{\cdot}7$ Å^3). The density calculated for four molecules per unit cell is 1·399 g./c.c.; the observed value is 1·405 g./c.c. The absorption coefficient is 59·6 cm.$^{-1}$ and no absorption correction was made because very small crystals (diam. 0·1—0·15 mm.) were used.

Equi-inclination Weissenberg photographs were taken with Cu-K radiation about the three principal axes for all layer lines up to (hk4), (4kl), and (h3l). A multiple-film technique was used and the intensities were estimated visually by comparison with a calibration slip. After corrections for Lorentz and polarisation factors had been applied, the intensities from different layer lines were correlated and their square roots extracted to give structure factors on an arbitrary scale; the scale factor required to make these values absolute was one of the parameters refined. For structure factors determined by each of us independently R was 0·076.

We thank Professor E. G. Cox, F.R.S., and Dr. D. W. J. Cruickshank for helpful discussions, and Miss D. E. Pilling for carrying out the computations on the Manchester University electronic computer. Some of the equipment used was purchased with grants from the Royal Society and Imperial Chemical Industries Limited, and part of the cost of the computing work was borne by a grant from the D.S.I.R.

Department of Inorganic and Structural Chemistry,
The University of Leeds. [*Received, February 11th*, 1958.]

[17] Davies and Hopkins, *Trans. Faraday Soc.*, 1957, **53**, 1563.
[18] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1939, p. 197.

518. *Evidence for the Existence of Hydrogen Dichloride Ions, HCl_2^-, in Organic Compounds.*

By D. W. A. Sharp.

The adducts formed by the action of hydrogen chloride on chlorotri-*p*-methoxyphenylmethane and 9-chloro-9-phenylxanthen have been examined by infrared and ultraviolet spectroscopy. The spectra have been compared with those of the corresponding carbonium salts and are in favour of the adducts' containing carbonium cations and hydrogen dichloride anions. The conditions for formation of carbonium hydrogen dichlorides are discussed and it is suggested that these anions may play an important part in organic reaction mechanisms.

Hydrogen dichloride ions, HCl_2^-, are formed by the addition of hydrogen chloride to pyridinium chloride,[1] tetramethylammonium chloride,[2] siliconium chlorides,[3] and cæsium chloride.[4] Since one requirement for the stabilisation of this ion in crystals appears to be a large cation, it was considered possible that carbonium ions might also stabilise it.

The formation of highly coloured adducts by the addition of hydrogen chloride to certain triarylchloromethanes is well known and, from a comparison of the colours of these adducts with the colours of the corresponding perchlorates, Gomberg and his co-workers [5, 6] concluded that the adducts contained a " quinocarbonium " grouping, that would now be called a carbonium ion. The present paper describes a spectroscopic study of these adducts.

Experimental

Tri-*p*-methoxyphenylmethane was obtained by Baeyer and Villiger's method; [7] it distilled at 270—280°/10 mm. Its oxidation gave the alcohol; [8] the hydrogen dichloride [5] was obtained by the action of gaseous hydrogen chloride on a solution of the alcohol in chloroform or benzene and acetyl chloride, followed by precipitation with light petroleum (b. p. 60—80°). Purification was effected by re-preparation (Found: C, 65·2; H, 6·0; Cl, 17·5. Calc. for $C_{22}H_{22}O_3Cl_2$: C, 65·2; H, 5·4; Cl, 17·55%). The dichloride was converted into the corresponding chloromethane by passing air through a refluxing benzene solution [5] (Found: C, 72·8; H, 5·1; Cl, 9·3. Calc. for $C_{22}H_{21}O_3Cl$: C, 71·6; H, 5·7; Cl, 9·65%); this chloromethane was obtained as faintly pink crystals, m. p. 161°, and its hydrolysis gave tri-*p*-methoxyphenylmethanol, m. p. 82·5°. The action of a solution of silver perchlorate in ether on an ethereal solution of chlorotri-*p*-methoxyphenylmethane gave tri-*p*-methoxyphenylmethyl perchlorate,[5] m. p. 198° after recrystallisation from chloroform–light petroleum.

Tri-*p*-methoxyphenylmethyl fluoroborate and hexafluorophosphate, both having m. p. 152° (decomp.), were prepared similarly; [9] they were obtained as red crystals but, like other carbonium salts of complex fluoro-acids,[9] did not give consistent analytical results. They were characterised by the weight of silver chloride precipitated during preparation [9] (Found for $C_{22}H_{21}O_3F_4B$: 0·98 equiv. Found for $C_{22}H_{21}O_3F_6P$: 0·96 equiv.).

9-Phenylxanthenol, m. p. 159°, was prepared by the action of phenylmagnesium bromide on xanthone.[10] Other derivatives were prepared as described by Gomberg and Cone [5] and as detailed above for the tri-*p*-methoxyphenylmethyl derivatives. Analyses and melting points recorded were: 9-phenylxanthenyl hydrogen dichloride (Found: C, 69·05; H, 4·7; Cl, 21·0.

[1] Kaufler and Kunz, *Ber.*, 1909, **42**, 385, 2482; Ephraim, *Ber.*, 1914, **47**, 1828.
[2] McIntosh and Steel, *Proc. Roy. Soc.*, 1904, **73**, 450; 1905, **74**, 320; Herbrandson, Dickerson, jun., and Weinstein, *J. Amer. Chem. Soc.*, 1954, **76**, 4046.
[3] Dilthey, *Ber.*, 1903, **36**, 923; *Annalen*, 1906, **344**, 300.
[4] West, *J. Amer. Chem. Soc.*, 1957, **79**, 4568.
[5] Gomberg and Cone, *Annalen*, 1909, **370**, 142.
[6] Gomberg and West, *J. Amer. Chem. Soc.*, 1912, **34**, 1529.
[7] Baeyer and Villiger, *Ber.*, 1902, **35**, 1197.
[8] Burton and Cheeseman, *J.*, 1953, 832.
[9] Sharp and Sheppard, *J.*, 1957, 674.
[10] Bünzly and Decker, *Ber.*, 1904, **37**, 2933.

Calc. for $C_{19}H_{14}Cl_2$: C, 69·3; H, 4·3; Cl, 21·6%); 9-chloro-9-phenylxanthen (Found: C, 78·7; H, 5·4; Cl, 11·7. Calc. for $C_{19}H_{13}Cl$: C, 77·9; H, 4·5; Cl, 12·1%); 9-phenylxanthenyl perchlorate, m. p. 282° (decomp.); *9-phenylxanthenyl fluoroborate*, m. p. 238° (decomp.) (1·00 equiv. of AgCl); *9-phenylxanthenyl hexafluorophosphate*, m. p. 225° (decomp.) (1·02 equiv. of AgCl).

Silver salts of complex fluoro-acids were prepared as previously described.[11] Cæsium hydrogen dichloride was obtained as needles by the action of hydrogen chloride on a solution of cæsium chloride in hydrochloric acid.[4]

All operations with chlorides and hydrogen dichlorides were carried out in the dry-box.

Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer, with rock-salt or fluorite optics. Mulls were prepared in Nujol or hexachlorobutadiene (in the dry-box if necessary).

Ultraviolet spectra were recorded on a Unicam S.P. 500 spectrophotometer. Chlorine compounds were studied in chloroform solution; reference spectra of carbonium ions were obtained from solutions of the appropriate alcohols in concentrated sulphuric acid.[12] Maxima and minima recorded were:

$(MeO{\cdot}C_6H_4)_2C{\cdot}OH$ in H_2SO_4: $\lambda_{max.}$ 494 (ε 114,000), $\lambda_{min.}$ 460 (ε 46,400), $\lambda_{max.}$ 455 mμ (ε 60,700).

$(MeO{\cdot}C_6H_4)_2C{\cdot}ClO_4$ in $CHCl_3$: $\lambda_{max.}$ 494 mμ (ε 31,400).

$(MeO{\cdot}C_6H_4)_2C{\cdot}HCl_2$ in $CHCl_3$: $\lambda_{max.}$ 490 mμ (ε 978).

9-Phenylxanthenol in H_2SO_4: $\lambda_{max.}$ 450 (ε 5620), $\lambda_{min.}$ 420 (ε 4310), $\lambda_{max.}$ 370 mμ (ε 24,900).

9-Phenylxanthenyl perchlorate in $CHCl_3$: $\lambda_{max.}$ 450 (ε 404), $\lambda_{min.}$ 420 (ε 330), $\lambda_{max.}$ 375 mμ (ε 2420).

9-Phenylxanthenyl hydrogen dichloride in $CHCl_3$: $\lambda_{max.}$ 460 (ε 36·9), $\lambda_{min.}$ 420 (ε 31·5), $\lambda_{max.}$ 380 mμ (ε 210).

Discussion

Possible structures for the hydrogen chloride adducts are: (1) The proton of the additional hydrogen chloride molecule is co-ordinated to the oxygen atom of the organic molecule, forming an oxonium chloride. (2) The extra hydrogen chloride molecule is loosely held in the organic lattice. (3) The extra hydrogen chloride molecule is co-ordinated to the carbonium ion. (4) The chloromethane is ionised, the extra hydrogen chloride molecule being co-ordinated to the resultant chloride ion. It should be possible to distinguish between these structures by a study of the infrared and ultraviolet spectra. In case (1) the symmetry of the molecule is locally altered, the remainder of the molecule still being similar in shape to the chloromethane: there should then be a change between the spectra of chlorotri-*p*-methoxyphenylmethane and its hydrogen chloride adduct. For cases (2) and (3) the spectra should be very similar to that of the corresponding chloromethane, the infrared spectrum of both adducts having an extra band due to absorption by the hydrogen chloride molecule. In case (4) the overall symmetry of the molecule has been completely altered and there should be a material change in the infrared spectrum.

Of the various compounds, tri-*p*-methoxyphenylmethane and 9-phenylxanthenol would be expected to have completely covalent character, with approximately tetrahedral bonding about the central carbon atom. The salts containing carbonium ions (perchlorates, fluoroborates, and hexafluorophosphates) should have approximately planar bonding about the " central " carbon atom: [9] that these salt contain identical carbonium

Anion	ClO_4^-	BF_4^-	PF_6^-
K^+ or Rb^+	1075, 1122 [13]	1032, 1058 [14]	845 [9]
$(p\text{-}MeO{\cdot}C_6H_4)_3C^+$	1100 (diffuse)	1060 (diffuse)	844
9-Phenylxanthenyl	1090	1052	842

ions is shown by the presence of a roughly constant spectrum for each cation with the spectrum of the appropriate anion superimposed. The anion spectra which have been

[11] Sharp and Sharpe, *J.*, 1956, 1855.
[12] Anderson, *J. Amer. Chem. Soc.*, 1935, **57**, 1673.
[13] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[14] Coté and Thompson, *Proc. Roy. Soc.*, 1952, *A*, **210**, 217.

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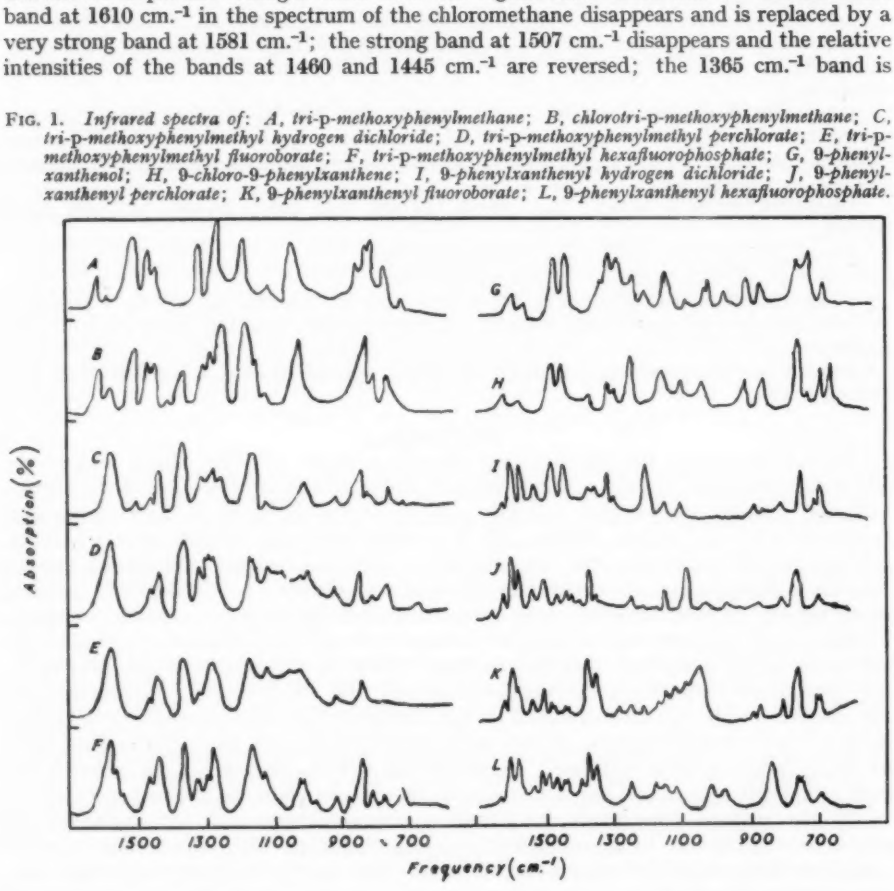
recorded are summarised in the Table which gives $\nu_{max.}$ in cm.$^{-1}$. Fig. 1 shows the relevant infrared spectra. The spectra of chlorotri-*p*-methoxyphenylmethane and 9-chloro-9-phenylxanthen are typical of "tetrahedral" molecules, but on addition of one equivalent of hydrogen chloride the spectra change and become more typical of carbonium structures.

To consider the two series of spectra in turn: for tri-*p*-methoxyphenylmethyl derivatives important changes occur over the region 1600—1200 cm.$^{-1}$. The moderate band at 1610 cm.$^{-1}$ in the spectrum of the chloromethane disappears and is replaced by a very strong band at 1581 cm.$^{-1}$; the strong band at 1507 cm.$^{-1}$ disappears and the relative intensities of the bands at 1460 and 1445 cm.$^{-1}$ are reversed; the 1365 cm.$^{-1}$ band is

FIG. 1. *Infrared spectra of: A, tri-*p*-methoxyphenylmethane; B, chlorotri-*p*-methoxyphenylmethane; C, tri-*p*-methoxyphenylmethyl hydrogen dichloride; D, tri-*p*-methoxyphenylmethyl perchlorate; E, tri-*p*-methoxyphenylmethyl fluoroborate; F, tri-*p*-methoxyphenylmethyl hexafluorophosphate; G, 9-phenylxanthenol; H, 9-chloro-9-phenylxanthene; I, 9-phenylxanthenyl hydrogen dichloride; J, 9-phenylxanthenyl perchlorate; K, 9-phenylxanthenyl fluoroborate; L, 9-phenylxanthenyl hexafluorophosphate.*



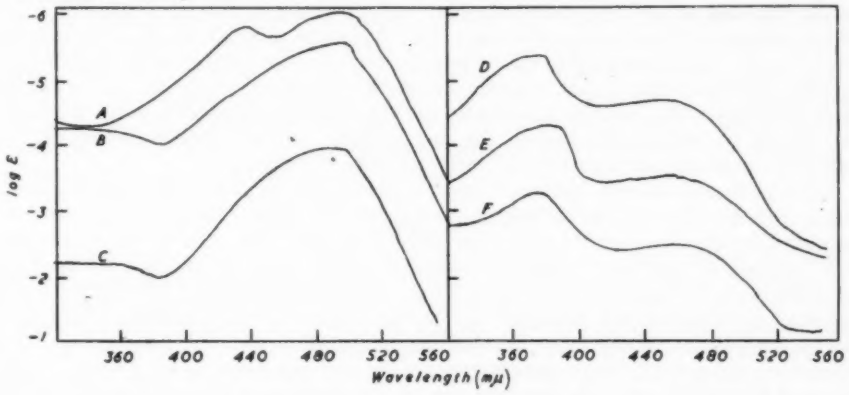
enhanced in intensity and a rather more complicated series of bands appears near 1300 cm.$^{-1}$. The spectrum of the hydrogen chloride adduct closely resembles those of the tri-*p*-methoxyphenylmethyl salts over this region, which contains the skeletal stretching vibrations of the aromatic ring systems.[15] The spectra cannot be completely compared with those obtained for the triphenylmethyl cation [9] since the methoxyl groups give rise to strong absorption in this region;[16] however, strong bands near 1580, 1360, and 1300 cm.$^{-1}$ are typical of carbonium ions.[9] The spectra over the range 1200—650 cm.$^{-1}$ again favour a carbonium structure for the hydrogen chloride adducts. The strongest

[15] Whiffen, *J.*, 1956, 1350.
[16] Briggs, Colebrook, Fales, and Wildman, *Analyt. Chem.*, 1957, **29**, 904.

band in this region is due to the aromatic C–H out-of-plane vibrations,[17] the shift of the peak from 825 to 845—850 cm.$^{-1}$ when the spectra of the covalent compounds are compared with those of the carbonium salts being in accordance with the increased electron-withdrawal from the ring in the latter compounds.[17]

For the 9-phenylxanthenyl derivatives the overall spectrum is more complex, as would be expected for a molecule of lower symmetry. Important changes do, however, occur on passing from 9-chloro-9-phenylxanthen to its hydrogen chloride adduct. The spectrum of the latter approximates to that of a carbonium salt at about 1600 cm.$^{-1}$, where a weak doublet in the " tetrahedral " compound is greatly enhanced in intensity. In its simplicity over the range 1150—650 cm.$^{-1}$ the spectrum is again typical of that from a carbonium salt. However, the presence of a strong doublet at 1485 and 1458 cm.$^{-1}$ in the spectrum of the hydrogen chloride adduct is more typical of the " tetrahedral " type of compound, whilst the strong band at 1205 cm.$^{-1}$ is not typical of either series. It cannot, therefore, be said that the infrared spectrum proves quite definitely a carbonium structure for the

FIG. 2. *Ultraviolet spectra of*: *A, tri-p-methoxyphenylmethanol in conc.* H_2SO_4; *B, tri-p-methoxyphenylmethyl perchlorate in* $CHCl_3$; *C, tri-p-methoxyphenylmethyl hydrogen dichloride in* $CHCl_3$; *D, 9-phenylxanthenol in conc.* H_2SO_4; *E, 9-phenylxanthenyl perchlorate in* $CHCl_3$; *F, 9-phenylxanthenyl hydrogen dichloride in* $CHCl_3$.



hydrogen chloride adduct of 9-chloro-9-phenylxanthen in the solid state, although much of the evidence favours this structure.

Further proof of the structure of these adducts could, in principle, be obtained from the infrared absorption of the HCl and HCl_2^- groupings. Hydrogen chloride absorbs [18] at 2886 cm.$^{-1}$ and very recently Waddington [19] has shown that the hydrogen dichloride ion in tetramethylammonium hydrogen dichloride absorbs at 1180 and 1565 cm.$^{-1}$. For cæsium hydrogen dichloride we have confirmed the presence of a band at 1180 cm.$^{-1}$ but could not find a band at 1565 cm.$^{-1}$. However, in the hydrogen chloride adducts of the chloromethanes, aromatic absorption would obscure any band at 1565 cm.$^{-1}$, and a band at 1180 cm.$^{-1}$ in the spectrum of a tri-*p*-methoxyphenylmethyl salt would also be obscured. It is possible that the 1205 cm.$^{-1}$ band in the spectrum of 9-phenylxanthenyl hydrogen dichloride is due to absorption by the HCl_2^- ion. The infrared spectrum of tri-*p*-methoxyphenylmethyl hydrogen dichloride over the range 3000—2500 cm.$^{-1}$ is almost identical with that of tri-*p*-methoxyphenylmethyl perchlorate and there can be no free hydrogen chloride in the lattice.

Thus, of the possible structures considered, infrared spectra definitely favour the

[17] Bellamy, *J.*, 1955, 2818; Kross, Fassel, and Margoshes, *J. Amer. Chem. Soc.*, 1956, **78**, 1332.
[18] Meyer and Levin, *Phys. Rev.*, 1929, **34**, 44.
[19] T. C. Waddington, personal communication.

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carbonium hydrogen dichloride postulate. Further evidence for this formulation for the adducts was sought by a study of the ultraviolet spectra of solutions but this work can only be considered complementary to the infrared results since the species present in solution are not necessarily those present in the solid state. Fig. 2 shows the ultraviolet spectra of solutions of the hydrogen chloride adducts in chloroform and compares them with those of the alcohols in concentrated sulphuric acid and solutions of the carbonium perchlorates in chloroform: the last two solutions are both expected to contain carbonium ions. In the positions of maxima and minima (for details see p. 2559) these spectra confirm the existence of carbonium ions in the solutions of the hydrogen chloride adducts, but in the intensity of absorption there are some unexplained discrepancies.

The existence of these salts containing hydrogen dichloride ions, HCl_2^-, gives rise to many interesting speculations since the only previous example of such an adduct has been the hydrogen difluoride ion, HF_2^-, where it has been postulated that the electronegative fluorine gives rise to a very strong hydrogen bond.[20] However, there is reason to suppose that the formation of such adducts is not even confined to hydrogen fluoride and chloride, the many highly coloured adducts of triarylmethyl salts with acids [21] indicating that the formation of such " bianions " is quite widespread.

Only those triarylchloromethanes which contain a large number of electron-releasing groups attached to the ring systems appear to form stable hydrogen dichlorides. Thus chlorotriphenylmethane forms an adduct with hydrogen chloride which decomposes at −45°,[22] and on substituting *p*-methoxyphenyl groups for phenyl it is only with chlorotri-*p*-methoxyphenylmethane that a stable, crystalline hydrogen dichloride can be isolated. Lund [23] considers that the chloromethanes are themselves ionised when there are four or more methoxyl groups attached to the ring systems, and chloromethanes which form hydrogen dichlorides certainly have an easily ionised C–Cl bond.

Since hydrogen chloride catalyses some organic reactions it is likely that carbonium hydrogen dichlorides take part in the reactions as intermediates, *e.g.*, in the isomerisation of camphene hydrochloride.[24,25] Hydrogen dichloride ions may also occur in reactions where hydrogen chloride is used as a condensing agent. For the reaction between *tert.*-butyl chloride and toluene, the proton-transfer mechanism proposed [26] was similar to that suggested by Sprauer and Simons [27] for the hydrogen fluoride-catalysed reaction. A possible mechanism for the latter involved an intermediate *tert.*-butyl cation but it was rejected on the ground that such carbonium ions had not been shown to exist. Since Olah and Kuhn [28] have shown the existence of complexes such as $C_6H_6Et^+BF_4^-$, formed by interaction of benzene, ethyl fluoride, and boron trifluoride, it seems possible to postulate intermediates such as $PhMe{\cdot}Bu^+HCl_2^-$ formed by interaction of toluene, butyl chloride, and hydrogen chloride.

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Inorganic Chemistry Laboratories, Imperial College of Science and Technology, South Kensington, London, S.W.7. [*Received, February 21st,* 1958.]

[20] Pauling, " The Nature of the Chemical Bond," 2nd edn., Cornell Univ. Press, New York, 1940.
[21] Schmidlin, " Das Triphenylmethyl," Enke, Stuttgart, 1914.
[22] Meyer, *Ber.*, 1908, **41**, 2576.
[23] Lund, *J. Amer. Chem. Soc.*, 1927, **49**, 1346.
[24] Bartlett and Pöckel, *ibid.*, 1938, **60**, 1585.
[25] Bartlett, " Organic Chemistry, an Advanced Treatise," Vol. III, Gilman (Editor), Wiley, New York, 1953, p. 66.
[26] Simons and Hart, *J. Amer. Chem. Soc.*, 1944, **66**, 1309.
[27] Sprauer and Simons, *ibid.*, 1942, **64**, 648.
[28] Olah and Kuhn, *Nature*, 1956, **178**, 1344.

519. *Kinetics and Mechanisms of Nucleophilic Displacement in Allylic Systems. Part IX.* Bimolecular Substitution with Rearrangement in the Reaction of* 1-tert.-*Butylallyl Chloride with Ethoxide Ion.*

By P. B. D. de la Mare, E. D. Hughes, P. C. Merriman, L. Pichat, and C. A. Vernon.

From 3-*tert.*-butylallyl alcohol (4 : 4-dimethylpent-2-en-1-ol) has been prepared 1-*tert.*-butylallyl chloride (3-chloro-4 : 4-dimethylpent-1-ene), together with its anionotropic isomer, from which it has been separated by fractional distillation. It has been characterised kinetically, and has been shown to give, on bimolecular reaction with ethoxide ions in ethanol, exclusively the product of substitution with anionotropic rearrangement, 3-*tert.*-butylallyl ethyl ether (4 : 4-dimethylpent-2-en-1-yl ethyl ether).

Early searches[1,2,3] for bimolecular substitution with anionotropic rearrangement (the S_N2' reaction), by using alkyl-substituted allyl chlorides and simple anions as the reactants, showed that the main and nearly exclusive product of such reaction was that of normal substitution. England and Hughes,[4] by using a tracer technique, showed, however, that the S_N2' reaction of 1-methylallyl bromide with bromide ions was slower than the corresponding S_N2 process by a factor of only about 40. From this it became clear that quite small structural changes might be sufficient to render dominant the reaction involving rearrangement, and for this reason the reaction of 1-*tert.*-butylallyl chloride, $CH_2{:}CH{\cdot}CHCl{\cdot}CMe_3$, was examined. In this compound, normal bimolecular substitution is impeded by steric factors analogous to those rendering this mode of substitution very slow in *neo*pentyl bromide.

Experimental

1- *and* 3-tert.-*Butylallyl Bromide.*—4 : 4-Dimethylpent-1-ene, prepared as described by Whitmore and Homeyer,[5] had b. p. 71·8°/756 mm., n_D^{25} 1·3892. This was treated in dry carbon tetrachloride with *N*-bromosuccinimide and benzoyl peroxide. When reaction was complete, succinimide was removed and the filtrate was fractionally distilled. Fractions, b. p. 60—62·5°/30 mm. (79% yield), from several experiments were combined and refractionated, giving material of b. p. 61·5—62°/28 mm., 53°/14 mm., n_D^{25} 1·4668, d_{25}^{25} 1·152. This was a mixture of 1- and 3-*tert.*-butylallyl bromide (3-bromo-4 : 4-dimethylpent-1-ene and 1-bromo-4 : 4-dimethylpent-2-ene) (Found: C, 47·9; H, 7·4; Br, 45·1. Calc. for $C_7H_{13}Br$: C, 47·5; H, 7·3; Br, 45·2%); there was no indication of separation during fractional distillation, but kinetic analysis, using excess of sodium ethoxide in ethanol, showed that the mixture contained 84% of 3-*tert.*-butylallyl bromide (k_2 at 24·9°, 0·138 l. mole^{-1} min.$^{-1}$) and 16% of the much more slowly reacting 1-*tert.*-butylallyl bromide.

1- *and* 3-tert.-*Butylallyl Alcohol.*—The mixture of bromides (100 g.) was hydrolysed by heating it under reflux for 3 hr. with water (2 l.), dioxan (3 l.), and potassium hydroxide (40 g.). Sodium chloride was then added to the cooled mixture; the organic layer was removed, dried (K_2CO_3), and fractionally distilled. The main products were two fractions: (*a*) b. p. 77·5°/152 mm. (60 g.) and (*b*) b. p. 85—86°/28 mm. (9 g.). Intermediate fractions were combined and worked up in successive experiments; the total overall yield of alcohols was about 90%. Refractionation gave the following materials; (a) 3-tert.-*butylallyl alcohol* (4 : 4-*dimethylpent*-2-*en*-1-*ol*), b. p. 77·5°/28 mm., 156—157°/760 mm., n_D^{25} 1·4360 (Found: C, 73·8; H, 12·7. $C_7H_{14}O$ requires C, 73·7; H, 12·3%) [α-*naphthylurethane*, m. p. 92·5° (Found: C, 76·9; H, 7·5; N, 5·1. $C_{18}H_{21}O_2N$ requires C, 76·3; H, 7·4; N, 5·0%); 3 : 5-dinitrobenzoate, m. p. 87·5°];

* Part VIII, *J.*, 1954, 4462.

[1] Roberts, Young, and Winstein, *J.*, 1942, **64**, 2157.
[2] Catchpole and Hughes, *J.*, 1948, 4; Catchpole, Hughes, and Ingold, *J.*, 1948, 8.
[3] Hughes, *Trans. Faraday Soc.*, 1941, **37**, 627.
[4] England and Hughes, *Nature*, 1951, **168**, 1002.
[5] Whitmore and Homeyer, *J. Amer. Chem. Soc.*, 1933, **55**, 4555.

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and (b) 1-*tert.*-butylallyl alcohol (4 : 4-dimethylpent-1-en-3-ol), b. p. 85·5°/152 mm., 131°/760 mm., n_D^{25} 1·4282, still impure even after being dried (K_2CO_3) (Found: C, 71·0; H, 11·9%), [α-*naphthylurethane*, m. p. 111·5° (Found: C, 75·8; H, 7·5; N, 4·8%)].

1- *and* 3-tert.-*Butylallyl Chloride*.—The properties of these materials have been outlined elsewhere,[6] but their preparation has not been described. 3-*tert.*-Butylallyl alcohol (50 g.) was cooled to 0°, and thionyl chloride (35 ml.) was added dropwise. The mixture was then stirred successively for 30 min. at 0°, for 1 hr. at room temperature, and for 1 hr. at 60°. The product was then treated with aqueous sodium carbonate and extracted with ether. After being dried, the ether layer was fractionated. The crude chloride, b. p. 53—64°, n_D^{25} 1·4373, was subjected to kinetic analysis. Samples of solution in 0·0963N-sodium ethoxide (0·0505N with respect to organic chloride, as determined by heating an aliquot part in a sealed tube with excess of aqueous nitric acid and silver nitrate) were heated at 64·0°, and at intervals the acid liberated was determined by titration, as follows:

Time (min.)	0	20	48	70	90	120	182	1120
Titre (ml. of 0·01656N-KOH)	10·83	13·25	15·88	16·85	17·83	18·71	19·60	20·34
x	—	2·42	5·05	6·02	7·00	7·88	8·77	9·51
k_2 (l. mole^{-1} min.$^{-1}$)	—	0·160	0·181	0·169	0·180	0·185	0·184	—

Here values of k_2 were calculated by using the value (9·51) of x at 1120 min. (about 25 half-lives) as the infinity for complete destruction of the rapidly reacting chloride. Further solvolysis was too slow to affect such a calculation. The total acid liberated on treatment with excess of silver nitrate was equivalent to $x = 16·31$ ml., so the material contained 60% of the more rapidly reacting 3-*tert.*-butylallyl chloride.

The mixture of chlorides obtained from several experiments was fractionally distilled under reduced pressure at high reflux ratio, through a helix-packed jacketed column. The separation was followed by b. p. (rising from 53° to 63·5° at 59 mm.) and refractive index (n_D^{25} rising from 1·4335 to 1·4390). A large quantity of material intermediate in properties was obtained. Suitable early and late fractions were combined and refractionated. The following materials were obtained: (a) 3-tert.-*butylallyl chloride* (1-*chloro*-4 : 4-*dimethylpent*-2-*ene*), b. p. 63·4°/58 mm., n_D^{25} 1·4389. Its reaction with sodium ethoxide went to completion (k_2 = 0·171 l. mole^{-1} min.$^{-1}$; 0·0977N-NaOEt, 65°) (Found: C, 63·3; H, 10·0; Cl, 26·3. $C_7H_{13}Cl$ requires C, 63·4; H, 9·8; Cl, 26·8%); (b) 1-tert.-*butylallyl chloride* (3-*chloro*-4 : 4-*dimethylpent*-1-*ene*), b. p. 54·7°/58 mm., n_D^{25} 1·4340 (Found: C, 64·2; H, 9·7; Cl, 26·4%). The latter material was shown by kinetic analysis to contain less than 3% of the more reactive isomer, which with 0·1N-sodium ethoxide at 65° reacted about 680 times more rapidly.

3-tert.-*Butylallyl Ethyl Ether*.—(a) *From* 3-tert.-*butylallyl chloride and sodium ethoxide*. The product, isolated in the usual way and distilled several times from molten potassium, had b. p. 152°/760 mm., n_D^{25} 1·4169.

(b) *From* 1-tert.-*butylallyl chloride and sodium ethoxide*. 1-*tert.*-Butylallyl chloride (10 g.) was allowed to react in sealed tubes for 2 hr. at 120° with saturated sodium ethoxide in ethanol. There were obtained 9 g. of 3-tert.-*butylallyl ethyl ether* (4 : 4-*dimethylpent*-2-*en*-1-*yl ethyl ether*), b. p. 152°/760 mm., n_D^{25} 1·4170 (Found: C, 75·6; H, 12·8. $C_9H_{18}O$ requires C, 76·2; H, 12·7%).

These two materials were characterised kinetically by reaction with bromine in acetic acid. The technique of measurement has been described elsewhere;[7] the rates were identical within experimental error, and about ten times faster than that for allyl ethyl ether.

(c) *By solvolysis of* 1-tert.-*butylallyl chloride*. 1-*tert.*-Butylallyl chloride (10 g.) and ethanol (250 ml.) were heated under reflux with precautions against ingress of water. The solution was prevented from becoming more than slightly acid by frequent addition of 0·3N-sodium ethoxide (lacmoid end-point). After 162 hr., reaction had virtually ceased. The product, recovered in the usual way, was 3-*tert.*-butylallyl ethyl ether (7 g.), n_D^{25} 1·4169, b. p. 147—148°/755 mm. (Found: C, 75·2; H, 12·7%).

1-tert.-*Butylallyl Ethyl Ether*.—To 1-*tert.*-butylallyl alcohol (8·3 g.) in diethyl ether (10 g.) a slight excess of finely powdered potassium was added. The mixture was heated under reflux for 4 hr., then cooled, and to it was added excess of ethyl iodide. The diethyl ether was removed by distillation, and the residue heated under reflux for 6 hr., after which time much potassium iodide had separated. The products were extracted with pentane and fractionally

[6] Vernon, *J.*, 1954, 423.
[7] de la Mare and Robertson, *J.*, 1945, 888.

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distilled to remove all the ethyl iodide. To the residue was added pyridine and phthalic anhydride; the mixture was heated for 8 hr. The hydrogen phthalate of any unchanged alcohol was then removed by extraction from pentane into aqueous alkali. The pentane extract was washed with acid and with water, dried, and fractionally distilled. The appropriate fractions of the product were distilled from metallic potassium and again fractionally distilled. The fraction, b. p. 121°, had n_D^{25} 1·3981 (Found: C, 77·8; H, 13·4%).

The infrared spectra of the various samples of ether were examined with a Grubb-Parsons double-beam recording infrared spectrophotometer. Those of the 3-*tert.*-butylallyl ether obtained in the three ways described above were identical, with a strong band at 976 cm.$^{-1}$, as is generally characteristic of *trans*-, but not of *cis*-1 : 2-disubstituted ethylenes, and weak or very weak bands at 996, 939, and 913 cm.$^{-1}$. That of the 1-ether was generally similar, though different in detail, but markedly different between 1000 and 900 cm.$^{-1}$, with strong bands at 1000, 973, and 923 cm.$^{-1}$; strong bands near 990 cm.$^{-1}$ and 910 cm.$^{-1}$ are generally characteristic [8] of monosubstituted ethylenes, R·CH:CH_2. Furthermore, groupings *trans*-R·CH=CHR and R·CH=CH_2 can usually be distinguished by the presence of weak bands near 1670 cm.$^{-1}$ and 1640 cm.$^{-1}$ respectively; [8] on the spectra which we have recorded, the 3-isomer had a weak band at 1678 cm.$^{-1}$, and the 1-isomer a band at 1639 cm.$^{-1}$.

Kinetics of Reaction of 1-tert.-*Butylallyl Chloride with Sodium Ethoxide.*—This reaction was of the first order with respect to organic chloride, and also with respect to ethoxide ions at high concentrations of sodium ethoxide; with 2·7M-NaOH, this kinetic form contributed *ca.* 90% to the total reactivity. The rate coefficients, corrected for the concomitant solvolysis, were k_2 (l mole^{-1} min.$^{-1}$) = 1·6 × 10^{-3} at 101°, 0·037 × 10^{-3} at 65·0°; E, 26 kcal. mole^{-1}.

Discussion

1- and 3-*tert.*-Butylallyl alcohol could be recognised and separated readily by fractional distillation. The halides were not easily separated but pure fractions could be recognised and characterised readily by kinetic methods. The formation of an equilibrium mixture of anionotropically related bromides is not unexpected,[9] in view of the great ease with which the corresponding methylallyl bromides undergo isomerisation.[10]

The reaction of 1-*tert.*-butylallyl chloride with sodium ethoxide is of the first order with respect to ethoxide ions provided that the concentration of ethoxide ions is sufficiently high. The reaction is very slow, as would be expected from the *neo*pentyl-like structure. However, the ratio of reactivities, 1-*tert.*-butylallyl chloride : 1-methylallyl chloride,[11] is *ca.* 1 : 100 at 65°, whereas the similar ratio for *neo*pentyl bromide to ethyl bromide is considerably larger (*ca.* 1 : 100,000 at 65°).[12] This agrees with the view that the reaction of 1-*tert.*-butylallyl chloride is not at the 1-carbon atom (S_N2) but involves attack on the less hindered olefinic 3-carbon atom (S_N2'), for otherwise differences resulting from steric hindrance should be, if anything, greater in the allyl than in the saturated system.

In accordance with this view, the product of the reaction is entirely that of abnormal substitution, and agrees in properties with that of authentic material prepared by reaction of ethoxide ions on 3-*tert.*-butylallyl chloride. We conclude that the reaction is of the S_N2' type.

The total rate [13] of the bimolecular reaction of sodium ethoxide with 3 : 3-dichloropropene at 65° is 0·84 × 10^{-3} l. mole^{-1} min.$^{-1}$, and roughly half of the reaction proceeds by the S_N2' route. The S_N2' reaction of 1-*tert.*-butylallyl chloride has a corresponding rate of 0·037 × 10^{-3} l. mole^{-1} min.$^{-1}$. Hence the 1-chloro-substituent in the former compound has a facilitating effect on the reaction, as compared with the 1-*tert.*-butyl group in the latter. This accords with the view that an important factor affecting such situations [14,15] is that a substituent may in some cases influence the rate of the S_N2' reaction

[8] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954.
[9] Cf. Djerassi, *Chem. Rev.*, 1948, **43**, 271.
[10] England, *J.*, 1955, 1615.
[11] Vernon, *J.*, 1954, 4462.
[12] Dostrovsky and Hughes, *J.*, 1946, 157.
[13] de la Mare and Vernon, *J.*, 1953, 3325.
[14] Hughes and Ingold, *J. Chim. phys.*, 1949, **45**, 236.
[15] de la Mare and Vernon, *J.*, 1953, 3555.

by attracting or repelling the π-electrons of the double bond and thereby facilitating or impeding the approach of a nucleophilic reagent to the unsaturated carbon atom.

The solvolysis of 1-*tert.*-butylallyl chloride also gives a product from which the recovered *tert.*-butylallyl ethyl ether is entirely the 3-isomer (as far as can be seen from its spectrum). This result differs from that obtained in the solvolysis of 1-methylallyl chloride; the latter reaction gives only 82% of 3-methylallyl ethyl ether.[3] The observation suggests that either (*a*) the solvolysis is bimolecular, or (*b*) steric congestion about the 1-carbon atom is sufficiently large even in the mesomeric carbonium ion as it is incipiently produced in the reaction to divert attack by solvent molecules predominantly to the 3-position.

We are indebted to Sir Christopher Ingold, F.R.S., for his interest in this work.

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520. *Experiments on the Synthesis of Diterpenes. Part I. A Total Synthesis of* (±)-*Totarol.*

By J. A. BARLTROP and N. A. J. ROGERS.

Some preliminary synthetical experiments on tricyclic diterpenoid resinols are described. The structure of the diterpenoid totarol has been confirmed as (I) by a total synthesis.

TOTAROL, a phenolic tricyclic diterpene, was first isolated from the wood of the Totara tree (*Podocarpus totara*) by Easterfield and McDowell.[1] A series of investigations by Short and his co-workers[2] led to the proposal that the structure (I) represented the constitution of totarol. An alternative structure (II), proposed by Brandt and Thomas,[3] which, unlike (I) obeys the isoprene rule, can be used as a basis for the interpretation of most of the chemical results but is difficult to reconcile with the spectroscopic data. Totarol has the infrared spectrum of a phenol possessing a very hindered hydroxyl group,[2] whereas the compound (II) would be expected to exhibit normal phenolic behaviour. Further, in the region 11·5—14·5 μ, totarol has the absorption expected of a 1 : 2 : 3 : 4- rather than a 1 : 2 : 3 : 5-tetrasubstituted benzene, as is shown in the Table.

Infrared spectra of totarol and related compounds in the region 11·5—14·5 μ.

Compound:	XV, R = OMe	XIII, R = OMe	XIV, R = OMe	XXIII [a]	IV	Totarol (I)
Band I	11·6, 11·8	11·75	11·7	11·65	11·8	—
Band II	12·5	—	—	12·55	—	12·52
Band III	—	12·8	12·75	—	12·8	—
Band IV	—	14·6	14·4	—	14·4	—

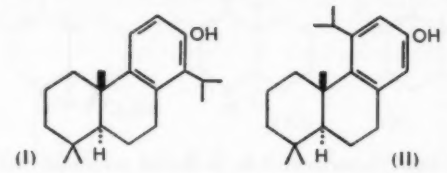
[a] Present authors' unpublished work.

Band I, which is associated with the out-of plane vibrational mode of a single aromatic C–H bond, and the bands III and IV which are associated with the corresponding mode for three adjacent aromatic C–H bonds, are seen to be absent in the spectrum of totarol, while band II, associated with the corresponding mode for two adjacent C–H bonds, is present.

A total synthesis of (±)-totarol, a preliminary account of which has been published,[4] confirms the spectroscopic assignments and shows that the diterpene has, in fact, the constitution (I).

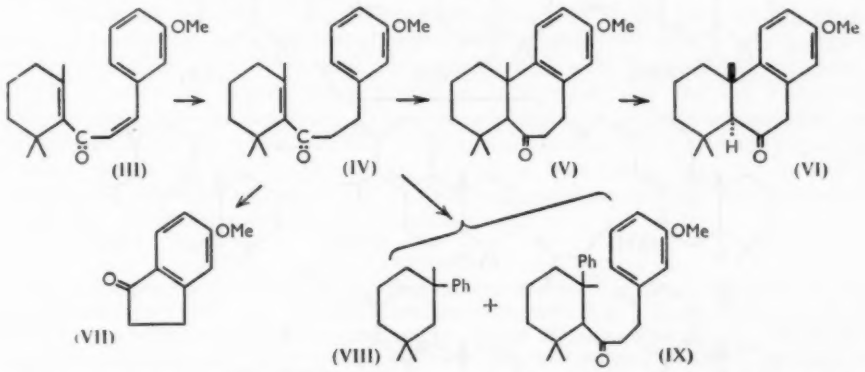
[1] Easterfield and McDowell, *Trans. New Zealand Inst.*, 1911, **43**, 55; 1915, **48**, 578.
[2] Short, Stromberg, and Wiles, *J.*, 1936, 319; Short and Stromberg, *J.*, 1937, 576; Short and Wang, *J.*, 1950, 991; 1951, 2979.
[3] Brandt and Thomas, *New Zealand J. Sci. Technol.*, 1951, **33**, *B*, 30.
[4] Barltrop and Rogers, *Chem. and Ind.*, 1957, 20.

We first tried to synthesise the tricyclic ketone (VI), in which, it was hoped, the 10-keto-function would ensure a *trans*-AB-ring-junction. The annexed route was chosen partly because of the ready availability of 2-acetyl-1 : 3 : 3-trimethyl*cyclo*hexene and *m*-methoxybenzaldehyde. These two substances readily gave the benzylidene derivative (III), which



was hydrogenated over Raney nickel to 2-(β-*m*-methoxyphenylpropionyl)-1 : 3 : 3-trimethyl*cyclo*hexene (IV). Several attempts were made to cyclise this compound, none of which gave the desired product (V). The use of aluminium chloride in nitrobenzene, saturated with hydrogen chloride, or of phosphoric acid at elevated temperatures [5] gave, as the main product, 5-methoxyind**an-1-one** (VII). With aluminium chloride in boiling benzene,[6] two products were obtained, probably 1 : 3 : 3-trimethyl-1-phenyl*cyclo*hexane (VIII) and 2-(β-*m*-methoxyphenylpropionyl)-1 : 3 : 3-trimethyl-1-phenyl*cyclo*hexane (IX). It is evident that the action of Lewis acids on the αβ-unsaturated ketone (IV) induces a reverse Darzens reaction, both products of this fission having been observed in the above reactions.

At this time it became clear that a 1- or 10-keto-function in an octahydrophenanthrene does not necessarily ensure a *trans*-AB-ring-junction. Indeed, there is now considerable evidence that Stork and Burgstahler's ketone [5] (X) is partly [7] or even largely [8] the AB-*cis*-compound. Further, the ketone (XI) obtained by Gutsche and Johnson [6]



was shown to be a mixture of *cis*- and *trans*-isomers, as was the keto-acid (XII) obtained by Parham, Wheeler, and Dodson.[6]

Attempts to synthesise the intermediate (XIV; R = MeO) from 2 : 2 : 6-trimethyl*cyclo*hexanone and 3-methoxyphenethylmagnesium bromide gave, as the principal products, 2 : 2 : 6-trimethyl*cyclo*hexanol, and 1 : 4-di-(*m*-methoxyphenyl)butane. Similar behaviour has been noted with other highly hindered ketones in the Grignard reaction.[9,10]

[5] Stork and Burgstahler, *J. Amer. Chem. Soc.*, 1951, **73**, 3544.
[6] Gutsche and Johnson, *ibid.*, 1946, **68**, 2239; Parham, Wheeler, and Dodson, *ibid.*, 1955, **77**, 1166.
[7] Saha, Ganguly, and Dutta, *Chem. and Ind.*, 1956, 412.
[8] Barltrop and Day, unpublished work.
[9] Conant and Blatt, *J. Amer. Chem. Soc.*, 1929, **51**, 1227; Johnson, Banerjee, Schneider, Gutsche, Shelberg, and Chinn, *ibid.*, 1952, **74**, 2841.
[10] King, King, and Topliss, *J.*, 1957, 573.

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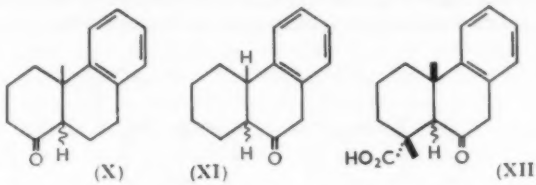
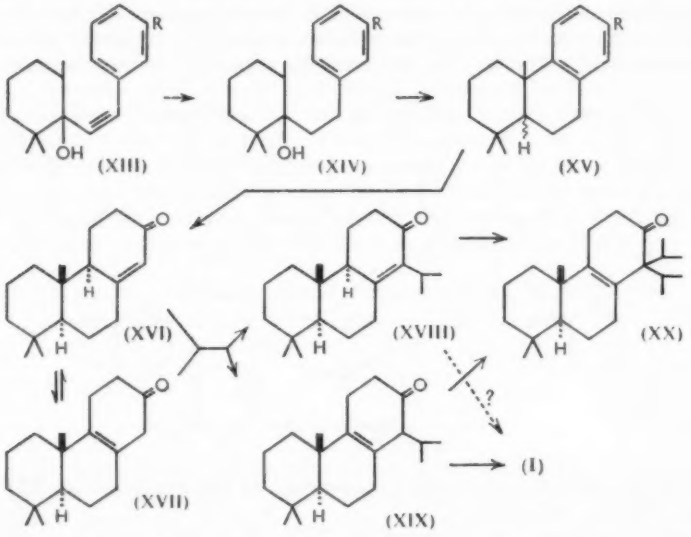
However, the reactions of several acetylenic derivatives with 2 : 2 : 6-trimethyl*cyclo*hexanone, to give the corresponding ethynylcarbinols in high yield, have been recorded;[10,11]



this ketone with potassium phenylacetylide in liquid ammonia indeed gave 2 : 2 : 6-trimethyl-1-phenylethynyl*cyclo*hexanol (XIII; R = H), in 50% yield. This was hydrogenated over 5% palladised charcoal to 2 : 2 : 6-trimethyl-1-phenethyl*cyclo*hexanol (XIV; R = H) in quantitative yield. Cyclisation with polyphosphoric acid afforded 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-1 : 1 : 12-trimethylphenanthrene (XV; R = H).

With potassium *m*-methoxyphenylacetylide, 2 : 2 : 6-trimethyl*cyclo*hexanone gave a high yield of the corresponding ethynylcarbinol (XIII; R = OMe). Hydrogenation over 5% palladised charcoal and then cyclisation with polyphosphoric acid gave *trans*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-7-methoxy-1 : 1 : 12-trimethylphenanthrene (XV; R = OMe). This substance readily crystallised after distillation. Chromatography on active alumina gave only one isolatable product, the infrared spectra of the fractions collected during this chromatography suggesting that the material was homogeneous

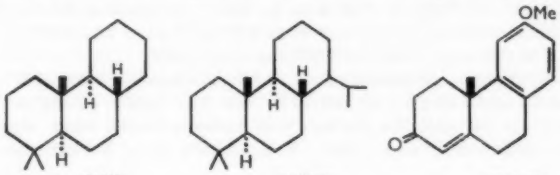


(cf. King *et al.*[10]). Reduction of this product with lithium in liquid ammonia[12] gave an enol ether, fission of which with dilute sulphuric acid, gave a mixture of podocarp-8(14)-(XVI) and podocarp-13(14)-en-7-one (XVII), which were separable by chromatography on alumina. The $\beta\gamma$-unsaturated ketone (XVII) was the only product isolated when the enol ether was hydrolysed with aqueous-alcoholic oxalic acid.[12]

[11] Campbell, *J. Amer. Chem. Soc.*, 1938, **60**, 2282; Sobotka and Chanley, *ibid.*, 1949, **71**, 4136; Milas, Macdonald, and Black, *ibid.*, 1948, **70**, 1829; Attenburrow, Cameron, Chapman, Evans, Jansen, and Walker, *J.*, 1952, 1094.

[12] Wilds and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5360, 5366

The dextrorotatory form of ketone (XVI) was obtained by Hosking,[13] and by Büchi and Jeger,[14] as a degradation product of the bicyclic diterpene manöol. A sample of the semicarbazone was kindly made available by Professor Jeger; its infrared spectrum, in Nujol mull, was very similar to that of the synthetic derivative, the slight differences being attributable to the small differences between the crystal structures of the (+)- and the (±)-compound. The low solubility of these substances rendered determination of their infrared spectra in solution impracticable, and a small quantity of the dextrorotatory



(XXI) (XXII) (XXIII)

material was therefore hydrolysed, the unsaturated ketone being obtained, in low yield, by chromatography of the product. The infrared spectrum of this material, in solution in carbon disulphide, was identical with that of the synthetic ketone (XVI).

Treatment of either isomer (XVI) or (XVII) with sodium *tert.*-amyloxide in benzene,[15] followed by refluxing under nitrogen with *iso*propyl iodide, gave a mixture of totar-8(14)-(XVIII) and totar-13(14)-en-7-one (XIX), the latter predominating. These ketones could not be separated by chromatography on alumina. That alkylation had occurred at position 8 and not at position 6 was shown by the position of the conjugated carbonyl band at 251 mμ.[16] Under more forcing conditions, 8-*iso*propyltotar-13(14)-en-7-one (XX) was obtained. [The nomenclature in this paper is based[17] on the hydrocarbons podocarpane (XXI) and totarane (XXII)].

Treatment of the mixture with *N*-bromosuccinimide in boiling carbon tetrachloride gave a bromo-ketone, or a mixture of bromo-ketones, which, on dehydrobromination in boiling γ-collidine, gave (±)-totarol (I), together with some ketonic material (largely XVIII). These were separated by careful chromatography on alumina, (±)-totarol being obtained as a colourless glass. The ultraviolet spectrum, and the infrared spectrum measured in carbon disulphide solution, were identical with those of (+)-totarol, a specimen of which was kindly provided by Dr. D. A. Peak of Boots Pure Drug Co. Ltd. The benzoates of synthetic and of (+)-totarol were also spectroscopically indistinguishable in both the ultraviolet and the infrared region.

Experimental

2-(β-m-*Methoxyphenylacryloyl*)-1 : 3 : 3-*trimethyl*cyclo*hexene* (III).—2-Acetyl-1 : 3 : 3-trimethyl*cyclo*hexene (3·42 g.), *m*-methoxybenzaldehyde (2·72 g.), and potassium hydroxide (0·56 g.) were heated under reflux for 30 min. in ethanol (30 c.c.). The mixture was acidified with acetic acid and most of the ethanol was removed under reduced pressure. The product was extracted with ether and washed with aqueous sodium carbonate and brine, dried, and distilled. The fraction of b. p. 165—175°/0·1 mm. was redistilled, to give the *acyl*cyclo*hexene* (3·49 g.), b. p. 166—169°/0·1 mm. (Found: C, 79·9; H, 8·4. $C_{19}H_{24}O_2$ requires C, 80·3; H, 8·4%).

2-(β-m-*Methoxyphenylpropionyl*)-1 : 3 : 3-*trimethyl*cyclo*hexene* (IV).—The above ketone (3·25 g.) in ethanol (40 c.c.) was hydrogenated under atmospheric pressure over Raney nickel. The reduction stopped after the uptake of 1·1 mols. of hydrogen. The filtered solution when distilled gave the *product* as a pale yellow liquid (2·75 g.), b. p. 185—190°/0·1 mm. (bath-temp.) (Found: C, 79·6; H, 9·0. $C_{19}H_{26}O_2$ requires C, 79·7; H, 9·1%).

[13] Hosking, *Ber.*, 1936, **69**, 780.
[14] Jeger, personal communication.
[15] Conia, *Bull. Soc. chim. France*, 1954, 690, 943.
[16] Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 72, 76.
[17] Klyne, *J.*, 1953, 3072.

Attempted Cyclisation of 2-(β-m-*Methoxyphenylpropionyl*)-1 : 3 : 3-*trimethyl*cyclo*hexene*.—(*A*) The ketone (5·72 g.) in nitrobenzene (50 c.c.) was saturated with dry hydrogen chloride. To the stirred solution was added finely powdered aluminium chloride (8·1 g.) and the stirring was continued for 20 hr. at room temperature. The mixture was poured on ice, and the nitrobenzene removed by steam-distillation. The residue was isolated with ether and distilled, to give 5-methoxyindan-1-one (VII) (1·01 g.), b. p. 145—150°/0·2 mm., which crystallised. Crystallisation from light petroleum and then benzene gave needles, m. p. 108° (Found: C, 73·7; H, 6·2. Calc. for $C_{10}H_{10}O_2$: C, 74·1; H, 6·2%) (semicarbazone, m. p. 237—238°) (Brandt and Horn,[18] and Ingold and Piggott [19] give m. p. 108°, and semicarbazone, m. p. 239°). The infrared spectrum had bands (μ) at 5·91 s, 7·98 s, 9·68 s, 12·35 m, and 14·1 m. The ultraviolet spectrum had bands at 266 ($\varepsilon_{max.}$ 2120) and 287 mμ ($\varepsilon_{max.}$ 1540).

(*B*) 2-(β-*m*-Methoxyphenylpropionyl)-1 : 3 : 3-trimethyl*cyclo*hexene (5·01 g.) was stirred with 90% phosphoric acid (50 c.c.) at 140—150° for 5 hr. under nitrogen. The pale brown mixture was poured on ice, and the product was extracted with ether, washed with sodium carbonate solution and water, and dried. Evaporation gave 5-methoxyindan-1-one (VII) (2·01 g.).

(*C*) The acyl*cyclo*hexene (10 g.) in pure dry benzene (120 c.c.) was added slowly, with stirring, to a boiling suspension of aluminium chloride (18 g.) in benzene (100 c.c.) through which a slow stream of dry hydrogen chloride was passed. The addition was complete in 1 hr., and stirring and treatment with hydrogen chloride were continued for 1 hr. longer. Stirring was continued for a further 2 hr. and the mixture was then poured on 2N-hydrochloric acid and ice. Isolation with ether followed by distillation gave three fractions: (*a*), b. p. 75—100°/0·2 mm., was redistilled to give 1 : 3 : 3-*trimethyl*-1-*phenyl*cyclo*hexane* (VIII) (0·2 g.), b. p. 78—83°/0·2 mm. (Found: C, 89·6; H, 10·1. $C_{15}H_{22}$ requires C, 89·1; H, 10·9%), whose infrared spectrum showed no carbonyl or ether absorption and had strong bands at 13·35 μ and 14·38 μ, the ultraviolet spectrum having a broad band system at *ca.* 260 mμ with peaks at 252 ($\varepsilon_{max.}$ 278), 257·5 ($\varepsilon_{max.}$ 283), 263·5 ($\varepsilon_{max.}$ 260), 267 ($\varepsilon_{max.}$ 238), and 282 mμ ($\varepsilon_{max.}$ 184). *Fraction* (*b*) (3·3 g.), b. p. 175—185°/0·2 mm., was redistilled, to give unchanged 2-(β-*m*-methoxyphenylpropionyl)-1 : 3 : 3-trimethyl*cyclo*hexene (IV), b. p. 175—180°/0·2 mm. *Fraction* (*c*) (2·2 g.), b. p. 195—205°/0·2 mm., was redistilled to give 2-(β-m-*methoxyphenylpropionyl*)-1 : 3 : 3-*trimethyl*-1-*phenyl*cyclo*hexane* (IX), b. p. 195—200°/0·2 mm. (Found: C, 82·1; H, 8·9. $C_{25}H_{32}O_2$ requires C, 82·4; H, 8·9%), whose infrared spectrum had bands at 5·87 s, 7·98 s, 9·68 s, 12·85 m, 13·25 s, and 14·35 sμ, the ultraviolet spectrum having bands at 215 ($\varepsilon_{max.}$ 13,100), 273 ($\varepsilon_{max.}$ 3460), and 280 mμ ($\varepsilon_{max.}$ 3400).

2 : 2 : 6-*Trimethyl*-1-*phenylethynyl*cyclo*hexanol* (XIII; R = H).—Phenylacetylene (2·44 g.) in anhydrous ether (30 c.c.) was added dropwise with stirring to a solution of potassamide (from 1·0 g. of potassium) in liquid ammonia (100 c.c.). After 10 min., 2 : 2 : 6-trimethyl*cyclo*hexanone (3·4 g.) in anhydrous ether (30 c.c.) was added dropwise and stirring was continued for 2 hr. Water was added and the product was extracted with ether, washed with brine, and distilled. 2 : 2 : 6-*Trimethyl*-1-*phenylethynyl*cyclo*hexanol* (2·47 g.) was collected at 153—156°/0·15 mm. (Found: C, 84·3; H, 9·3. $C_{17}H_{22}O$ requires C, 84·3; H, 9·1%).

2 : 6 : 6-*Trimethyl*-1-*phenethyl*cyclo*hexanol* (XIV; R = H).—2 : 2 : 6-Trimethyl-1-phenylethynyl*cyclo*hexanol (2·45 g.) in ethyl acetate (70 c.c.) was hydrogenated over 5% palladised charcoal (0·5 g.) at 1 atm. and room temperature. When the uptake of hydrogen had ceased, the solution was filtered and distilled. 2 : 6 : 6-*Trimethyl*-1-*phenethyl*cyclo*hexanol* was obtained as a colourless oil (2·40 g.), b. p. 172—177°/0·1 mm. (bath-temp.) (Found: C, 82·3; H, 10·4. $C_{17}H_{26}O$ requires C, 82·9; H, 10·6%).

1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro*-1 : 1 : 12-*trimethylphenanthrene* (XV; R = H).—2 : 2 : 6-Trimethyl-1-phenethyl*cyclo*hexanol (2·3 g.) was stirred with 90% phosphoric acid (20 c.c.) and phosphoric oxide (25 g.) under dry nitrogen for 45 min. at 95°, then cooled, poured into water (200 c.c.), and extracted with ether. The extract was washed with brine, dried, and distilled. 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro*-1 : 1 : 12-*trimethylphenanthrene* (1·6 g.) obtained had b. p. 108—110°/0·05 mm. (Found: C, 89·0; H, 10·5. $C_{17}H_{24}$ requires C, 89·5; H, 10·5%).

1-(m-*Methoxyphenylethynyl*)-2 : 2 : 6-*trimethyl*cyclo*hexanol* (XIII; R = MeO).—*m*-Methoxyphenylacetylene (9·8 g.) in anhydrous ether (90 c.c.) was slowly added with stirring to a solution

[18] Brandt and Horn, *J. prakt. Chem.*, 1927, **115**, 351.
[19] Ingold and Piggott, *J.*, 1923, 1469.

of potassamide (from 3·75 g. of potassium) in liquid ammonia (450 c.c.). After 10 min., 2 : 2 : 6-trimethyl*cyclo*hexanone (9·8 g.) in dry ether (90 c.c.) was added dropwise and stirring was continued for 1 hr. The mixture was worked up in the usual way, to give 1-(m-*methoxyphenylethynyl*)-2 : 2 : 6-*trimethyl*cyclo*hexanol* (15·75 g.), b. p. 180—185°/0·1 mm. (Found: C, 79·0; H, 8·8. $C_{18}H_{24}O_2$ requires C, 79·4; H, 8·8%).

1-(m-*Methoxyphenethyl*)-2 : 2 : 6-*trimethyl*cyclo*hexanol* (XIV; R = MeO).—1-(*m*-Methoxyphenylethynyl)-2 : 2 : 6-trimethyl*cyclo*hexanol (15·7 g.) was reduced as above, to give 1-(m-*methoxyphenethyl*)-2 : 2 : 6-*trimethyl*cyclo*hexanol* (15·5 g.), b. p. 210—212°/0·15 mm. (bath-temp.) (Found: C, 78·8; H, 10·0. $C_{18}H_{28}O_2$ requires C, 78·3; H, 10·2%).

trans-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro-7-methoxy*-1 : 1 : 12-*trimethylphenanthrene* (XV; R = OMe).—1-(3-Methoxyphenethyl)-2 : 2 : 6-trimethyl*cyclo*hexanol (10·0 g.) was stirred under nitrogen with syrupy phosphoric acid (120 c.c.) and phosphoric oxide (150 g.) for 45 min. at 85°. The mixture was worked up in the usual way, to give trans-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro-7-methoxy*-1 : 1 : 12-*trimethylphenanthrene* (7·93 g.) (a pale violet fluorescence), b. p. 155—160°/0·1 mm., needles, m. p. 52—55° (Found: C, 83·7; H, 10·1. $C_{18}H_{26}O$ requires C, 83·7; H, 10·1%).

Chromatography of 0·5 g. of the product on active alumina (60 g.) gave only one isolatable product. The m. p.s and infrared spectra of the fractions collected during this chromatography were identical.

Podocarp-8(14)-(XVI) *and podocarp*-13(14)-*en*-7-*one* (XVII).—*trans*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-7-methoxy-1 : 1 : 12-trimethylphenanthrene (XV; R = OMe) (7·93 g.) in anhydrous ether (400 c.c.) was added to liquid ammonia (1 l.) and treated with lithium metal (3·5 g.; 15 atoms per mole) in small pieces with stirring. Stirring was continued for 10 min. and then ethanol (50 c.c.) was added dropwise during 20 min. When the reaction was complete and the ammonia had evaporated, the mixture was diluted with water (500 c.c.), and the product isolated with ether. A colourless oil (7·02 g.) was obtained, the infrared spectrum of which showed only very weak bands attributable to starting material.

(*A*) The crude reduction product (3·5 g.) was heated to 60° for 30 min. with ethanol (150 c.c.) and 5N-hydrochloric acid (120 c.c.), then poured into ice-water and worked up in the usual way, to give a pale yellow oil (2·7 g.). This was chromatographed on a column of alumina (250 g.) which had been deactivated with 5% w/v of 10% aqueous acetic acid. Elution with light petroleum (b. p. 40—60°) gave unchanged *trans*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-7-methoxy-1 : 1 : 12-trimethylphenanthrene (720 mg.). Further elution with 10% benzene in light petroleum gave successively podocarp-13(14)- (XVII) (780 mg.) and *podocarp*-8(14)-*en*-7-*one* (XVI) (897 mg.). The latter rapidly solidified and recrystallisation from light petroleum gave the pure αβ-unsaturated ketone, m. p. 89—90° (Found: C, 82·7; H, 10·2. $C_{17}H_{24}O$ requires C, 82·9; H, 10·6%), $\lambda_{max.}$ 241·5 mμ (ε 16,150). The semicarbazone had m. p. 213—215° (decomp.).

(*B*) The crude reduction product (3·5 g.) in ethanol (200 c.c.) was treated with oxalic acid (7·5 g.) and water (10 c.c.) at 25° for 40 min., then poured into water (500 c.c.) and worked up in the usual manner, to give a colourless oil which was chromatographed on deactivated alumina (350 g.). Elution with light petroleum gave unchanged *trans*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-7-methoxy-1 : 1 : 12-trimethylphenanthrene (700 mg.). Further elution with 10% benzene in light petroleum gave *podocarp*-13(14)-*en*-7-*one* (XVII) (2·65 g.) which separated from light petroleum in crystals, m. p. 101—103° (Found: C, 82·7; H, 11·0%).

Isomerisation of Podocarp-13(14)-*en*-7-*one* (XVII).—The ketone (530 mg.) was heated at 90° with ethanol (20 c.c.) and 5N-hydrochloric acid (15 c.c.) for 30 min. The mixture was worked up in the usual way. The infrared spectrum of the crude product indicated the presence of both starting material and the αβ-unsaturated ketone (XVI). Chromatography on deactivated alumina (30 g.) gave unchanged podocarp-13(14)- (170 mg.) and podocarp-8(14)-en-7-one (195 mg.).

Proof of Identity of Synthetic Podocarp-8(14)-*en*-7-*one with the* (+)-*Compound*.—The infrared spectra of (+)- and (±)-podocarp-8(14)-en-7-one semicarbazone in Nujol mull were identical apart from the following slight differences: (+)-isomer, 13·15, 12·25, 9·21, 7·55 μ; (±)-isomer, 13·18, 12·27, 9·16, 7·53 μ. The (+)-semicarbazone (16·1 mg.) was heated under reflux for 20 min. with 2N-hydrochloric acid (5 c.c.) and ethanol (1 c.c.). The mixture was diluted with water, and the product was isolated with ether. The pale yellow oil (11·7 mg.) had an infrared spectrum which indicated some isomerisation to the 13(14)-isomer (bands at 5·8 and 5·98 μ).

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The mixture was chromatographed on deactivated alumina (1·5 g.). Elution with 1 : 1 benzene–light petroleum gave (+)-podocarp-8(14)-en-7-one (2·0 mg.) which slowly crystallised. The infrared spectrum of this ketone, in CS_2, proved identical in all respects with that of the synthetic material measured under the same conditions.

Totar-8(14)- (XVIII) *and Totar*-13(14)-*en*-7-*one* (XIX).—(*A*) Podocarp-8(14)-en-7-one (XVI) (415 mg.) in *iso*propyl bromide (8 c.c.; 50 mol.) was treated with a M-solution of sodium *tert.*-amyloxide in dry benzene (15 c.c.; 10 mol.), under dry nitrogen. The mixture was heated under reflux for 3½ hr., cooled, and shaken with 2N-hydrochloric acid (25 c.c.). The product was isolated with ether and chromatographed on deactivated alumina (40 g.). Elution with benzene gave a pale yellow viscous oil (175 mg.), b. p. 155—160°/0·05 mm. (bath-temp.) (Found: C, 83·5; H, 11·0. $C_{20}H_{32}O$ requires C, 83·3; H, 11·1%). The infrared spectrum had bands at 5·85 and 6·0 μ, showing that both totar-8(14)- and totar-13(14)-en-7-one were present. Very little change in the composition of the mixture was achieved by chromatography on alumina. The ultraviolet spectrum had a band at 251 mμ (ε 6900).

(*B*) A mixture of podocarp-8(14)- and -13(14)-en-7-one (760 mg.) in *iso*propyl iodide (7 c.c.; 40 mol.) was treated with M-sodium *tert.*-amyloxide in dry benzene (20 c.c.; 10 mol.) under dry nitrogen and heated under reflux for 2½ hr. A deep red colour was produced on warming which gradually disappeared as sodium iodide was precipitated. After acidification with 2N-sulphuric acid (10 c.c.) the product, a yellow oil (705 mg.), was isolated with ether and chromatographed on deactivated alumina (70 g.). Elution with light petroleum gave 8-*iso*-*propyltotar*-13(14)-*en*-7-*one* (XX) (267 mg.), b. p. 165—170°/0·1 mm. (bath-temp.) (Found: as 83·9; H, 11·3. $C_{23}H_{38}O$ requires C, 83·6; H, 11·5%). Further elution with 1 : 1 benzene–light petroleum gave a mixture of totaren-7-ones (202 mg.).

(*C*) Podocarp-13(14)-en-7-one (680 mg.) in *iso*propyl iodide (2·5 c.c.; 15 mol.) was treated C, above, with M-sodium *tert.*-amyloxide (7·5 c.c.; 5 mol.), refluxing being continued for 1 hr. The product was a pale yellow oil (690 mg.) which, on distillation, gave a mixture of totaren-7-ones (Found: C, 82·9; H, 11·3%).

(±)-*Totarol* (I).—The synthetic mixture of totaren-7-ones (420 mg.) and freshly prepared *N*-bromosuccinimide (290 mg.; 1·1 mol.) were heated together under reflux in dry carbon tetrachloride for 30 min., then cooled, filtered, washed with 10% sodium carbonate solution, and evaporated. A pale yellow viscous oil was obtained which when heated to 100° in a vacuum lost some hydrogen bromide. A glass (400 mg.) remained which was heated under reflux with redistilled γ-collidine (15 c.c.) for 2½ hr. The bulk of the γ-collidine was removed in a vacuum, 5N-hydrochloric acid (15 c.c.) added, and the product isolated with ether. The residual clear brown glass (380 mg.), the infrared spectrum of which showed, in addition to those bands expected for (±)-totarol, a weak band at 5·85 μ and a moderately intense band at 6·0 μ, was chromatographed on deactivated alumina (40 g.). Elution with light petroleum gave 118 mg. of ketone. Further elution with 1 : 1 benzene–light petroleum gave a pale yellow glass (182 mg.) the infrared spectrum of which showed that very little ketone was present. The fractions containing least ketonic material (83 mg.) were rechromatographed on active alumina (10 g.). Elution with 1 : 1 benzene–light petroleum gave a mixture of totaren-7-ones (15·8 mg.). Further elution with benzene gave (±)-*totarol* (35·3 mg.), b. p. 170—175° (bath-temp.)/0·2 mm. (Found: C, 84·4; H, 10·4. $C_{20}H_{30}O$ requires C, 83·9; H, 10·5%), whose infrared spectrum, in CS_2, was identical with that of (+)-totarol. The ultraviolet spectrum had a band at 278 (ε 1970) and a shoulder at 285 mμ (ε 1910). (+)-Totarol had a band at 278 (ε 1980) and a shoulder at 285 mμ (ε 1915). (±)-*Totaryl benzoate* was a glass, b. p. 145—150° (bath-temp.)/2 × 10^{-5} mm. (Found: C, 83·5; H, 9·0. $C_{27}H_{34}O$ requires C, 83·1; H, 8·9%), whose infrared spectrum in CS_2 was identical with that of (+)-totaryl benzoate (m. p. 144—145°). The ultraviolet spectra of the racemic and the dextrorotatory materials were identical ($\lambda_{max.}$ 220 mμ, ε 21,000; 228 mμ, ε 20,000; shoulder at 265 mμ, ε 3300).

We are grateful to Professor O. Jeger for a specimen of the semicarbazone of the degradation product (XVI) and to Dr. D. A. Peak for a sample of (+)-totarol.

Dyson Perrins Laboratory, Oxford University. [*Received, May 28th*, 1957.]

521. *The Direct Introduction of the Diazonium Group into Aromatic Nuclei. Part IV.*[1] *The Preparation of Diazonium Salts from Phenols.*

By J. M. Tedder and G. Theaker.

A wide variety of phenolic compounds have been found to react with buffered nitrous acid, to yield diazonium salts. The reaction, which proceeds *via* the nitrosophenol, shows all the usual characteristics of electrophilic substitution. The reaction stops at the nitrosophenol (quinone monoxime) stage when the parent quinone is particularly stable, as in the naphthols. Phenols, treated with hydrogen chloride and an alkyl nitrite dissolved in the corresponding alcohol, yield diazonium salts derived from the related alkyl phenyl ether.

The direct introduction of the diazonium group into phenols by treatment with an excess of nitrous acid or its derivatives first reported in the 1870's,[2] has been encountered several times since, usually as an unwanted side reaction.[3,4,5,6,7] Curiously no attempt has been made to develop this process, and when *ortho*- or *para*-diazonium salts have been required they have been prepared from the appropriate aminophenol by the usual diazotisation procedure. The present paper describes the development of a practical method of preparing diazonium salts directly from phenols, often in good yield.

Three of the previous papers report deliberate attempts to prepare diazonium salts by treating phenols with excess of nitrous acid. Rodionow and Matweew[3] obtained diazonium salts from phenol-*o*- and -*p*-sulphonic acid in 78% and 52% yield respectively. Morel and Sisley[4] prepared *p*-hydroxyphenylazo-β-naphthol in 80% yield simply by treating phenol with excess of hydrochloric acid and sodium nitrite and coupling with β-naphthol. Philpot and Small[6] claim to have obtained a 60% yield of (2-hydroxy-5-methylphenylazo)-β-naphthol from *p*-cresol. In fact *ortho*-diazo-oxides couple extremely slowly with β-naphthol and the product reported by Philpot and Small is a mixture of the dye with much unchanged β-naphthol. However, using their conditions and coupling with resorcinol led to a 25% yield of (2-hydroxy-5-methylphenylazo)resorcinol. It would

Table 1. p-*Cresol treated with an excess of nitrous acid at* 0° *in aqueous acetone.* (*Yields represent dye obtained by coupling with resorcinol.*)

Reagents (moles/mole of C_7H_8O)		Time	Yield
HCl	$NaNO_2$	(hr.)	(%)
2	2	19	14
5	5	25	31
10	15	67	34
4	14·5	19	71

be expected that *p*-cresol would be less reactive than phenol, and Hodgson and Crouch[8] found that conditions which yielded nitroso-derivatives from *o*- and *m*-cresol yielded only 4-hydroxy-3-nitrotoluene from *p*-cresol. The present investigation was commenced by estimating the yields of diazonium salt obtained from *p*-cresol under a variety of conditions. Some of these results are recorded in Table 1. It will be seen that only moderate yields were obtained until a solution containing a very large excess of sodium nitrite and only a small excess of hydrochloric acid was used. These conditions were then adopted as standard for the main investigation with other phenols. The excess of nitrite acts as a buffer and a constant pH (3—4) is maintained. In order to obtain a homogeneous

[1] Part III; Tedder, *J. Amer. Chem. Soc.*, 1957, **79**, 6090.
[2] Weselsky, *Ber.*, 1871, **4**, 613; 1875, **8**, 98.
[3] Rodionow and Matweew, *Ber.*, 1924, **57**, 1711.
[4] Morel and Sisley, *Bull. Soc. chim. France*, 1927, **41**, 1217.
[5] Hodgson, *J.*, 1931, 1494; 1932, 866.
[6] Philpot and Small, *Biochem. J.*, 1938, **32**, 534.
[7] Kraaijeveld and Havinga, *Rec. Trav. chim.*, 1954, **73**, 537, 549.
[8] Hodgson and Crouch, *J.*, 1943, 221.

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solution 15—50% of acetone was added, depending on the solubility of the phenol. Nitrous acid evaporates slowly from the solution throughout the experiment, but in all the experiments reported there was still excess at the end.

These simple conditions have proved very effective for the preparation of diazonium salts from a number of phenols (see Table 2). For the most reactive compounds yields of over 90% of crude azo-dye were obtained. The crude dyes in all cases proved to be essentially single compounds (*i.e.*, one isomer was obtained to the virtual exclusion of the

TABLE 2. *Yields of azoresorcinol dyes obtained from different phenols* (0·01 *mole*) *in buffered nitrous acid* ($NaNO_2$ 0·145 *mole*; HCl 0·05 *mole*.)

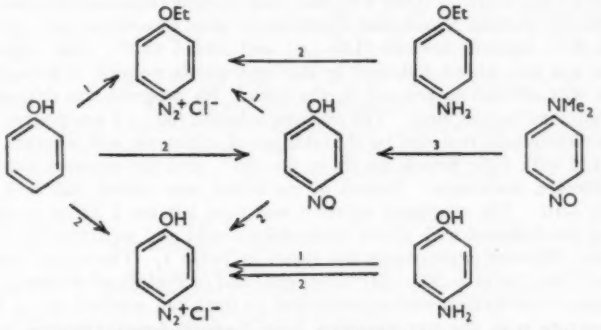
Phenol	Time (hr.)	Temp.	Solvent: Acetone (c.c.)	Solvent: Water (c.c.)	Yield (%)	Remarks
Phenol	19	0°	50	100	96	
o-Cresol	18	0	50	100	98	
m- ,,	19	0	50	100	98	
p- ,,	43	0	50	100	77	71% after 19 hr.
m-Chlorophenol	23	20	50	100	95	
p- ,,	73	20	50	100	63	48·5% after 27½ hr.
p- ,,	260	0	50	100	34	4% after 17 hr., 16% after 91 hr.
o-Nitrophenol	96	20	50	60	42	32·5% after 20 hr.
m- ,,	96	20	25	100	0·6	
p- ,,	96	20	25	100	7	
m-HO·C_6H_4·CHO	26	20	20	100	13	
p- ,,	26	20	20	100	49	
p-HO·C_6H_4·SO_3H	42	20	—	150	—	50% of azo-β-naphthol dye
α-Naphthol	17	0	75	100	Trace	80% of 4-nitroso-1-naphthol
β- ,,	18	0	75	100	3·0	78% of 1 nitroso-2-naphthol
3 : 2-HO·$C_{10}H_6$·CO_2H	24	20	30	100	18	

others) and usually in quite a high degree of purity [*e.g.*, the crude dye from *m*-cresol was found to contain over 87% of (4-hydroxy-2-methylphenylazo)resorcinol by spectral analysis]. Deactivating groups hinder the reaction and in general the results are exactly what would be expected from a normal electrophilic substitution. *p*-Cresol, *p*-chlorophenol, *m*-nitrophenol, and *m*-hydroxybenzaldehyde, where the directing influence of the second substituent is in opposition to the directing effect of the hydroxyl, all give much lower yields than their isomers where the directing effects are complementary. The naphthols give practically no diazonium salt, although good yields of the nitroso-compounds were obtained. The explanation of this seems to lie in the stability of the corresponding quinones, so that the nitrosonaphthols exist almost exclusively in the quinone monoxime forms which fail to react further. Support for this idea is given by the behaviour of 3-hydroxy-2-naphthoic acid, which may be expected to have a higher electrode potential [9] and gives a moderate yield of diazonium salt.

In Part I of this series the preparation of *p*-hydroxybenzenediazonium chloride in aqueous ethanol is described. When a similar reaction was attempted with *m*-cresol in an entirely anhydrous alcoholic medium, a diazonium salt was formed, but the β-naphthol dye prepared from it was insoluble in alkali. It was discovered that *O*-alkylation had accompanied the introduction of the diazo-group and to prevent confusion a preliminary note was published.[10] A more detailed study of this reaction has now been carried out. Phenol, dissolved in dry ethanol and treated with five mols. of hydrogen chloride and five mols. of ethyl nitrite at 0° for 160 hours, yielded 58·5% of *p*-ethoxybenzenediazonium chloride and 9% of *p*-hydroxybenzenediazonium chloride as estimated by the β-naphthol coupling products. The annexed scheme shows a series of related reactions, some of which have previously been reported, the rest of which have been carried out in order to establish at which stage the *O*-alkylation had occurred; these results indicate that it is either the intermediate nitrosophenol that is alkylated or that alkylation occurs during

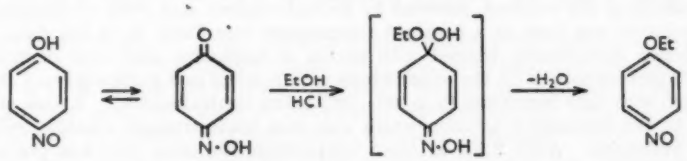
[9] Fieser and Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 491.
[10] Tedder and Theaker, *Chem. and Ind.*, 1957, 1485.

the conversion of the nitrosophenol into the diazonium salt. The former is the more probable since Havinga, Kraaijeveld, and Schors [11] have shown that nitrosophenols are alkylated in alcoholic hydrogen chloride. Evidence that it is the quinone monoxime form which undergoes alkylation is provided by the preparation of 26% of 2-ethoxynaphthalene-1-diazonium chloride from β-naphthol in an alcoholic medium, while only 3% of the



Reagents: 1, EtO·NO–HCl–EtOH. 2, $NaNO_2$–HCl–H_2O. 3, NaOH.

2-hydroxynaphthalene-1-diazonium salt could be obtained in an aqueous medium because of the stability of the quinone monoxime (see above). To show that the reaction occurs with other alcohols as well as other phenols, *p-iso*pentyloxybenzenediazonium salt was



prepared from phenol, *iso*pentyl nitrite, and hydrogen chloride in *iso*pentyl alcohol solution.

The reactions described in this paper provide a really practical method of preparing diazonium salts from the more reactive phenols. For large-scale work it would probably be possible to omit the acetone, provided there was adequate stirring. A study has also been made of the behaviour of aromatic hydroxy-acids in similar buffered nitrous acid solutions, but because these reactions have complications of their own they will be reported separately.

Experimental *

p-Cresol: *Philpot and Small's Work * Repeated.*—*p*-Cresol (0·86 g.) was dissolved in a mixture of concentrated hydrochloric acid (10 c.c.) and water (40 c.c.), diluted to 1 l., and treated with 4N-sodium nitrite (10 c.c.). The mixture was kept at 20° in the dark for 1 hr., and then rendered strongly alkaline and treated with β-naphthol (2 g.). Coupling was allowed to proceed for 1 hr., then the mixture was extracted with ethyl acetate. The extract was washed with dilute sodium hydroxide solution, dried, and evaporated, to leave pale grey-purple crystals (1·20 g.), m. p. 108—110°, shrinking at 100°. This material, designated (2-hydroxy-5-methylphenylazo)-β-naphthol by Philpot and Small was in fact largely unchanged β-naphthol. By repeated

* It has been found that the original standardised thermometer in the m. p. apparatus used throughout this work had been removed and replaced by another which read approximately 1·5—2·0° low. This must have occurred at an early stage of the work and affects *all* m. p.s in Parts II and III, and ref. 10, and *some* of those in Part I. All m. p.s reported in the present paper have been redetermined with a freshly standardized thermometer.

[11] Havinga, Kraaijeveld, and Schors, *Rec. Trav. chim.*, 1955, **74**, 1256.

recrystallisation from methanol a small quantity of red needles was obtained, having m. p. 219—221° alone or in admixture with (2-hydroxy-5-methylphenylazo)-β-naphthol (m. p. 221°) prepared from 2-amino-5-methylphenol (Found: C, 73·0; H, 5·2; N, 10·2. Calc. for $C_{17}H_{14}O_2N_2$: C, 73·4; H, 5·1; N, 10·1%). The experiment was repeated and the diazonium solution coupled with resorcinol (see below). The yield of crude dye, 0·48 g. (m. p. 207—211°), corresponded to a 24·5% conversion [authentic (2-hydroxy-5-methylphenylazo)resorcinol had m. p. 217° (decomp.), see below]. After 6 hr. the yield of crude resorcinol dye was 1·0 g. (51·5%).

p-*Cresol*: *Effect of Sodium Nitrite and Hydrochloric Acid Concentrations.*—*p*-Cresol (1·08 g.) was dissolved in 2 : 1 aqueous acetone (150 c.c.) and cooled to 0°. The appropriate weight of sodium nitrite was also added, followed by the appropriate volume of 2N-hydrochloric acid, and the reaction was allowed to proceed in the dark. Its progress was determined by withdrawing 50 c.c. portions for coupling. The reacting solution (50 c.c.) was poured on ice (100 g.), and the excess of nitrous acid removed by the addition of sulphamic acid solution. The solution was then extracted with light petroleum (b. p. 60—80°), and the aqueous residue neutralised with sodium hydrogen carbonate. Excess of resorcinol was added, followed by 2N-sodium hydroxide to pH ~10. The combined solution was then left for 2 hr. at room temperature, then the dye was precipitated with dilute hydrochloric acid and separated by filtration. The yields of dye from different experiments are listed in Table 1. The crude dye from the last experiment in the Table has m. p. 203—210° (decomp.) and recrystallised from aqueous methanol, to yield (2-hydroxy-5-methylbenzeneazo)resorcinol as dark red needles, m. p. 217° (decomp.) alone or in admixture with the dye prepared from 2-amino-4-methylphenol by diazotisation (Found: C, 63·6; H, 4·7; N, 11·4. Calc. for $C_{13}H_{12}O_3N_2$: C, 63·9; H, 5·0; N, 11·5%). The colour of the dye in concentrated sulphuric acid was yellow-brown, becoming orange on dilution with water.

General Method for the Preparation of Diazonium Salts from Phenols.—The phenol (0·01 mole) was dissolved in a mixture of acetone and water (see Table 2). Sodium nitrite (0·145 mole) was added to this solution, followed by 2N-hydrochloric acid (0·04—0·05 mole), and the combined solution was kept at a constant temperature (see Table 2) in the dark. Samples were withdrawn periodically, treated with excess of sulphamic acid, and neutralised with sodium hydrogen carbonate [in the experiments with *p*-cresol and *p*-chlorophenol the solution was extracted with light petroleum (b. p. 60—80°) before neutralisation]. Excess of resorcinol was added to the neutralised solution which was then made strongly alkaline (pH ~10) by 2N-sodium hydroxide. After 2 hr. at room temperature the crude dye was precipitated by dilute hydrochloric acid. The crude dyes were isolated by filtration (yields in Table 2) and their individual properties and purification are described below.

Phenol.—The crude dye, m. p. 218—219°, recrystallised from aqueous alcohol in dark red needles, m. p. 226—227° (decomp.) (4-hydroxybenzeneazoresorcinol,[12] m. p. 226°), $\lambda_{max.}$ 386 mμ (in EtOH) (Found: C, 62·4; H, 4·5; N, 11·9. Calc. for $C_{12}H_{10}O_3N_2$: C, 62·6; H, 4·4; N, 12·2%). The dye dissolves in concentrated sulphuric acid to a yellow-brown solution which becomes orange on storage or on dilution.

o-*Cresol.*—The crude dye, m. p. 194—198°, when recrystallised from aqueous methanol yielded two products. The principal fraction (86%) was a red powder, m. p. 206—207° (decomp.), $\lambda_{max.}$ 385 mμ (in MeOH) (Found: C, 63·3; H, 5·2; N, 11·1. $C_{13}H_{12}O_3N_2$ requires C, 63·9; H, 5·0; N, 11·5%). The *dye* gives a yellow-brown colour in concentrated sulphuric acid (orange brown on dilution). The other, less soluble dye, a *mononitro-compound* (~5%, crude), formed red-brown needles, m. p. 218—219° (decomp.) (Found: C, 53·8; H, 4·4. $C_{13}H_{11}O_5N_3$ requires C, 54·0; H, 3·8%), $\lambda_{max.}$ 390 mμ.

m-*Cresol.*—The crude dye, m. p. 196—199°, recrystallised from aqueous methanol, yielded (*4-hydroxy-2-methylphenylazo*)*resorcinol* as red-brown needles, m. p. 208° (decomp.) alone or in admixture with the dye prepared from 4-amino-3-methylphenol by normal diazotisation. The pure dye had $\lambda_{max.}$ 390 mμ (in MeOH), and gave an orange-green colour in concentrated sulphuric acid (orange on storage or dilution) (Found: C, 63·8; H, 5·2; N, 11·6. $C_{13}H_{12}O_3N_2$ requires C, 63·9; H, 5·0; N, 11·5%).

m-*Chlorophenol.*—The crude *dye*, m. p. 212—217° (decomp.), recrystallised from aqueous ethanol, yielded red-brown needles, m. p. 237—238° (decomp.); it gave a yellow-brown colour in concentrated sulphuric acid (orange on dilution) (Found: C, 54·7; H, 3·7; N, 10·4. $C_{12}H_9N_2O_3Cl$ requires C, 54·5; H, 3·4; N, 10·6%).

[12] Borsche and Frank, *Annalen*, 1926, **450**, 75.

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p-*Chlorophenol*.—The crude *dye* from a sample withdrawn after 91 hr. at 0°, had m. p. 232—237°; it recrystallised from aqueous methanol as yellow-brown needles, m. p. 244—245° (decomp.) (Found: C, 55·0; H, 3·7; N, 10·8. $C_{12}H_9O_3N_2Cl$ requires C, 54·5; H, 3·4; N, 10·6%), and gave a brown colour in concentrated sulphuric acid (orange on dilution). The experiment was repeated with the same quantities at 20°: results were similar.

o-*Nitrophenol*.—Recrystallisation of the crude *dye*, m. p. 213—216°, from acetone gave orange plates, m. p. 218—219° (decomp.), $\lambda_{max.}$ 386 mμ (in EtOH), giving an orange-yellow colour in concentrated sulphuric acid (Found: C, 52·6; H, 3·8; N, 15·1. $C_{12}H_9O_5N_3$ requires C, 52·4; H, 3·3; N, 15·3%).

m-*Nitrophenol*.—The crude dye had $\lambda_{max.}$ 477 mμ (in EtOH) and gave an orange colour in concentrated sulphuric acid. It was not characterised further.

p-*Nitrophenol*.—Recrystallisation of the crude dye, m. p. 264—266° (decomp.), from aqueous methanol gave yellow needles, m. p. 263—265° (decomp.), $\lambda_{max.}$ 402 mμ (in EtOH), giving a yellow-orange colour in concentrated sulphuric acid which deepened on dilution (Found: C, 52·2; H, 3·7; N, 15·1%).

m-*Hydroxybenzaldehyde*.—The crude *dye* (m. p. indefinite, decomp. >215°) recrystallised from aqueous acetone as orange needles, indefinite m. p., decomp. >217°, $\lambda_{max.}$ 500 mμ (in EtOH) (Found: C, 60·6; H, 4·3. $C_{13}H_{10}O_4N_2$ requires C, 60·5; H, 3·9%). A solution of the dye gave a precipitate with 2 : 4-dinitrophenylhydrazine hydrochloride solution. The dye dissolved in concentrated sulphuric acid to an orange-red solution.

p-*Hydroxybenzaldehyde*.—The crude *dye*, m. p. 220° (decomp.), recrystallised from ethyl methyl ketone as orange needles, indefinite m. p., decomp. >220°, $\lambda_{max.}$ 437 mμ (in EtOH) (Found: C, 60·5; H, 4·1; N, 11·0. $C_{13}H_{10}N_2O_4$ requires C, 60·5; H, 3·9; N, 10·9%), giving an orange-yellow colour in concentrated sulphuric acid. The 2 : 4-dinitrophenylhydrazone was prepared and proved hard to purify: it had m. p. 274—277° (decomp.), $\lambda_{max.}$ 428 mμ (in EtOH), and gave an orange solution in concentrated sulphuric acid and a purple colour in sodium hydroxide.

p-*Hydroxybenzenesulphonic Acid*.—Potassium *p*-hydroxybenzenesulphonate (2·12 g.) was treated in water (150 c.c.) with sodium nitrite (10 g.) and 2N-hydrochloric acid (25 c.c.) at 20°. After 18 hr. at 20° a sample (50 c.c.) was withdrawn, treated with sulphamic acid to remove the excess of nitrous acid, made alkaline, and treated with β-naphthol. After 2 hr. the mixture was acidified, then neutralised again with sodium hydrogen carbonate. The resulting mixture was extracted with ether, to remove the excess of β-naphthol, and the aqueous residue was re-acidified to liberate the free dye (0·33 g.). After 42 hr. another sample was withdrawn, and the yield of dye was 0·49 g. The dye recrystallised from aqueous ethanol; it had no m. p.; $\lambda_{max.}$ were 548 mμ (0·021 g./l. in $NaHCO_3$ solution) and 518 mμ (0·002 g./l.). The sodium salt of the authentic dye, (2-hydroxy-5-sulphophenylazo)-β-naphthol, prepared from 2-amino-4-sulphophenol, had $\lambda_{max.}$ 548 mμ (0·0175 g./l.) and 515 mμ (0·002 g./l.). Holmes [13] has reported $\lambda_{max.}$ 548 mμ (2·0 g./l.) and 515 mμ (0·002 g./l.). The free acid dye formed a nickel complex on treatment with nickel chloride in aqueous ethanol. The complex, which recrystallised from aqueous ethanol as bronze needles, had no definite m. p. but decomposed above 270°; it had $\lambda_{max.}$ 528 mμ (0·012 g./l. in EtOH) (Found: C, 42·9; H, 4·5; N, 5·9; Ni, 6·7; H_2O, 15·7. $C_{32}H_{22}O_{10}N_4S_2,8H_2O$ requires C, 43·2; H, 4·3; N, 6·3; Ni, 6·6; H_2O, 16·2%). The nickel complex from the authentic dye had similar properties and $\lambda_{max.}$ 529 mμ (0·012 g./l.).

α-*Naphthol*.—α-Naphthol (1·44 g.) was dissolved in acetone (75 c.c.) and water (100 c.c.) and then treated with sodium nitrite (10 g.) and 2N-hydrochloric acid (20 c.c.) at 0—2°. After a short time an orange product separated. The reaction was continued for 17 hr., then the precipitate was filtered off (0·5 g.; m. p. 186—189°). It recrystallised from aqueous methanol as orange-brown needles, m. p. 198—199° (4-nitroso-1-naphthol,[14] m. p. 198°). The filtrate was treated with sulphamic acid to remove the excess of nitrous acid, then extracted with carbon tetrachloride. Evaporation of the extract left a residue of further 4-nitroso-1-naphthol (0·85 g.). The main aqueous residue was neutralised, treated with resorcinol, and made strongly alkaline. Some colour developed, but the yield of dye was too small for isolation on reacidification.

β-*Naphthol*.—β-Naphthol (1·44 g.) was treated as in the previous experiment. After 18 hr. a similar precipitate was filtered off (0·35 g.; m. p. 100—105°) and recrystallised from aqueous

[13] Holmes, *Ind. Eng. Chem.*, 1924, **16**, 36.
[14] Meyer and Lenhardt, *Annalen*, 1913, **398**, 79.

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methanol to yield material of m. p. 107—109° alone or on admixture with 1-nitroso-2-naphthol (lit.,[15] 109·5°). The filtrate was treated with sulphamic acid and extracted as before. The carbon tetrachloride extract yielded further crude nitrosonaphthol (1·0 g.). The aqueous residue, coupled with resorcinol as above, gave a small yield of a crude dye (0·08 g.).

Reaction in Alcoholic Media.—Phenol in ethanol. Phenol (0·94 g.) was treated in dry ethanolic 2·6N-hydrogen chloride (20 c.c.) at 0° with ethyl nitrite (3·75 c.c.). After 48 hr. at 0°, a sample (10 c.c.) was withdrawn and poured on ice. The mixture was extracted with ether, and the aqueous residue neutralised and coupled with β-naphthol. The dye was isolated by chloroform-extraction, and the extract washed with dilute sodium hydroxide solution; the washings containing unchanged β-naphthol and hydroxyphenylazo-β-naphthol were retained. Evaporation of the chloroform left the crude alkylated dye (0·49 g., 40·5%), m. p. 121—123°, which recrystallised from methanol to yield *p*-ethoxyphenylazo-β-naphthol as orange-red needles, m. p. 130—131° alone or in admixture with material prepared from *p*-phenetidine (Charrier and Ferreri [16] report m. p. 132°). The alkaline washings (above) were acidified and extracted with chloroform. The extract was concentrated and the hydroxyphenylazo-β-naphthol separated from unchanged β-naphthol by chromatography on alumina. The β-naphthol was eluted with ether, leaving the dye which was then washed out with methanol. The crude dye (0·06 g., 5·5%), m. p. 181—185°, recrystallised from aqueous ethanol to yield *p*-hydroxyphenylazo-β-naphthol, m. p. and mixed m. p. 191—193°, $\lambda_{max.}$ 418 mμ (in C_6H_6). Evaporation of the original ether extract (above) left a dark oil (0·15 g., 39% of the starting material), smelling strongly of phenol. The oil was redissolved in ether and extracted with dilute aqueous sodium hydroxide. The aqueous layer was shaken with benzoyl chloride, to yield phenyl benzoate which after recrystallisation from methanol had m. p. and mixed m. p. 66—67°. Evaporation of the ether left a trace of uncharacterised fragrant oil. After 7 days at 0° another sample was withdrawn and treated similarly; the yields of alkylated and free phenolic dye were 58·5% and 9·1% respectively.

Phenol in iso*pentyl alcohol.* Phenol (0·94 g.) was dissolved in a 4·7N-solution of hydrogen chloride in *iso*pentyl alcohol (21 c.c.) and then treated with *iso*pentyl nitrite (6·7 c.c.) at 20°. The mixture quickly became brown and some heat was evolved. After 4 hr. at 15—20° 10 c.c. were withdrawn and poured on ice. The mixture was extracted with ether, and the aqueous layer neutralised and coupled with β-naphthol. The alkylated *dye* (0·20 g., 17%), m. p. 100—102°, was isolated as above. Recrystallisation from methanol yielded red needles, m. p. 110—111°, which gave a magenta-coloured solution in concentrated sulphuric acid (Found: C, 75·6; H, 6·8; N, 8·2. $C_{21}H_{22}O_2N_2$ requires C, 75·4; H, 6·6; N, 8·4%). Only traces of the non-alkylated dye were obtained.

β-*Naphthol in ethanol.* β-Naphthol (0·35 g.) was treated in dry ethanolic 5·1N-hydrogen chloride (12 c.c.) at 0° with ethyl nitrite (1 c.c.). The reaction was allowed to continue for 28 hr. at 0° before the mixture was poured on ice and extracted with ether. The aqueous layer was coupled with β-naphthol, and the crude blue-black dye (0·22 g., 26·5%), m. p. 160—180°, isolated as before. The dye was purified with difficulty from aqueous ethanol; the pure *product* had no sharp m. p., decomposition setting in above 161°; it gave a blue colour in concentrated sulphuric acid (Found: C, 77·5; H, 5·2; N, 7·5. $C_{22}H_{18}O_2N_2$ requires C, 77·2; H, 5·3; N, 8·2%) and had $\lambda_{max.}$ 529 mμ (in C_6H_6). Only a trace of non-alkylated dye was obtained.

p-*Aminophenol diazotised in ethanol.* *p*-Aminophenol hydrochloride (0·73 g.) was suspended in ethanolic 2·6N-hydrogen chloride (15 c.c.) and treated with ethyl nitrite (1 c.c.) at 0°. After 1½ hr. the mixture was poured on ice and coupled with β-naphthol. No alkylated product was obtained: all the dye, m. p. 190—193°, was soluble in dilute sodium hydroxide solution.

Phenetole in ethanol. Phenetole (0·3 g.) was dissolved in ethanolic 2·6N-hydrogen chloride (6 c.c.) and treated with ethyl nitrite (1 c.c.) at 0°. After 24 hr. the mixture was poured on ice, and the aqueous portion coupled with β-naphthol. A trace of dye was formed (0·005 g.); it was entirely alkylated.

p-*Nitrosophenol in ethanol.* *p*-Nitrosophenol (0·62 g.) was dissolved in ethanolic 2·6N-hydrogen chloride (15 c.c.) and treated with ethyl nitrite (1 c.c.) at 0°. After 26 hr. the mixture was poured on ice, and the diazonium salts were coupled with β-naphthol as previously. A mixture of dyes (0·75 g.; m. p. 70—90°) was obtained, all alkylated. The mixture was

[15] Stenhouse and Groves, *J.*, 1877, **32**, 50.
[16] Charrier and Ferreri, *Gazzetta*, 1911, **41**, 728.

separated by chromatography on alumina, elution being with benzene–light petroleum (b. p. 90—120°). Three bands separated, the centre band containing the major product. The front band was not identified with certainty. Only a trace of product was isolated (m. p. 134—136°; $\lambda_{max.}$ 478 mμ in C_6H_6); it gave a purple-red colour in concentrated sulphuric acid. It may have been (2-chloro-4-ethoxyphenylazo)-β-naphthol which [17] melts at 140°. The centre band and main product was *p*-ethoxyphenylazo-β-naphthol, m. p. and mixed m. p. 131°. The top band was obtained as red needles, m. p. 129—130° (mixed m. p. with centre band 100—105°), $\lambda_{max.}$ 483 mμ (in C_6H_6), and gave a blue-purple colour in concentrated sulphuric acid. It was believed to be a bisazo-derivative, but was not characterised further.

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THE UNIVERSITY, SHEFFIELD, 10. [*Received, December 20th*, 1957.]

[17] Hurst and Thorpe, *J.*, 1915, **107**, 940.

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522. *Synthetic Studies in the Diterpene Series. Part I. Synthesis of Some Degradation Products of Methyl Totaryl Ether.**

By D. NASIPURI and A. C. CHAUDHURI.

The phenanthrene derivatives (II), (III), and (IV) are synthesised. They are identical with those obtained by Short and Wang [1] as the dehydrogenation products of methyl totaryl ether, substantiating the structure of the latter.

THE structure of totarol [1] (I) was elucidated by Short and his co-workers,[2,3] mainly by dehydrogenation of totarol and its derivatives and has been confirmed by total synthesis.[4] By milder dehydrogenation, Short and Wang [2] obtained three products (II, III, and IV) from methyl totaryl ether, none of which, however, was synthesised. Since the structure (I) does not conform to the isoprene rule, it appeared desirable to synthesise these products and the following is an account of the synthetical operations.

3-Methoxy-2-*iso*propylbenzonitrile [6] (VI; R = CN) was converted into the amide (VI; R = $CO{\cdot}NH_2$) by 30% hydrogen peroxide in alkali,[7] then into the iodo-compound (VI; R = I) by Hofmann degradation [8] followed by diazotisation and into the alcohol (VI; R = $CH_2{\cdot}CH_2{\cdot}OH$) by the action of ethylene oxide on the Grignard reagent of the iodo-compound in an overall yield of 15—16%. The derived bromide (VI; R = $CH_2{\cdot}CH_2Br$) was condensed with ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate (V) in the usual way, to give the product (VII) in satisfactory yield. The latter on cyclodehydration [5] and subsequent hydrolysis furnished γ-(2-carboxy-3 : 4-dihydro-6-methoxy-5-*iso*propyl-1-naphthyl)butyric acid (VIII) in about 60% yield, the dimethyl ester of which on Dieckmann cyclisation and hydrolysis gave 1 : 2 : 3 : 4 : 9 : 10-hexahydro-7-methoxy-1-oxo-8-*iso*propylphenanthrene (IX). The ketone was condensed with methylmagnesium iodide, and the resultant alcohol on simultaneous dehydration and dehydrogenation by 30% palladium–charcoal [9] afforded 2-methoxy-8-methyl-1-*iso*propylphenanthrene (IV) in good yield. The properties of this compound and the corresponding phenol and their

* Part of this work was published in *Science and Culture*, 1957, **23**, 319.

[1] Easterfield and McDowell, *Trans. New Zealand Inst.*, 1911, **43**, 55; 1915, **48**, 578.
[2] Short and Wang, *J.*, 1951, 2979.
[3] Short and Stromberg, *J.*, 1937, 516; Short and Wang, *J.*, 1950, 991.
[4] Barltrop and Rogers, *Chem. and Ind.*, 1957, 397.
[5] Bardhan and Nasipuri, *J.*, 1956, 350.
[6] (*a*) Richtzenhain and Nippus, *Ber.*, 1944, **77**, 566; (*b*) Fuson, Gaertner, and Chadwick, *J. Org. Chem.*, 1948, **13**, 489.
[7] *Org. Synth.*, Coll. Vol. II, 1st edn., p. 586.
[8] Wallis and Lane, *Org. Reactions*, Vol. III, p. 267.
[9] Linstead and Thomas, *J.*, 1940, 1127.

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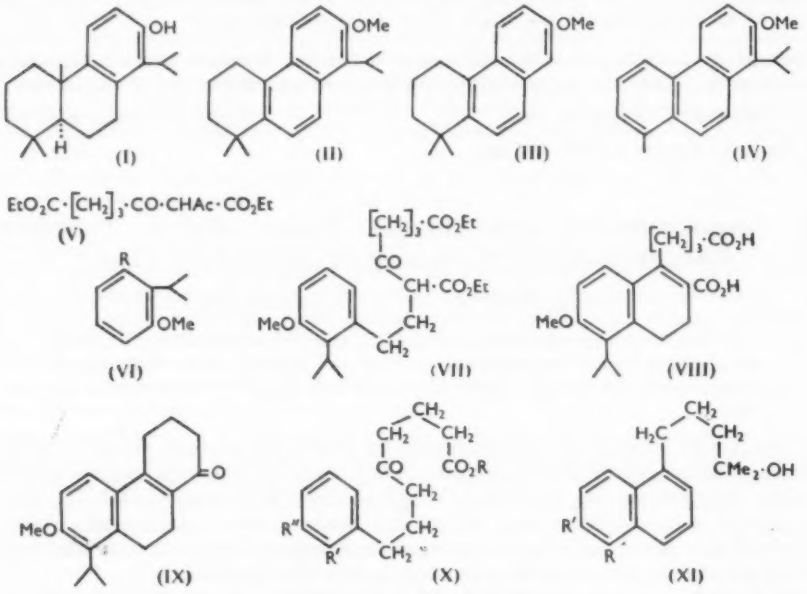
derivatives corresponded with those recorded by Short and Wang [1] for their compound C from methyl totaryl ether.

As a model for the synthesis of the other two compounds (II and III), we treated methyl γ-1-naphthylbutyrate with an excess of methylmagnesium iodide. Heating the resultant alcohol (XI; R = R′ = H) with polyphosphoric acid [10] gave an excellent yield of a liquid hydrocarbon, 1 : 2 : 3 : 4-tetrahydro-1 : 1-dimethylphenanthrene, which was characterised



by dehydrogenation to 1-methylphenanthrene. This route was next extended to the synthesis of 1 : 2 : 3 : 4-tetrahydro-7-methoxy-1 : 1-dimethylphenanthrene (III). Methyl 8-*m*-methoxyphenyl-5-oxo-octanoate [11] (X; R = Me, R′ = H, and R″ = OMe) was conveniently obtained by alkylation of ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate with *m*-methoxyphenethyl bromide followed by hydrolysis and esterification. The resultant methyl γ-6-methoxy-1-naphthylbutyrate afforded the phenanthrene derivative (III), identical with compound B of Short and Wang.[2] This compound was aromatised to 7-methoxy-1-methylphenanthrene, the main dehydrogenation product of methyl totaryl ether under more vigorous conditions.[2]

Finally, the keto-ester (VII) was hydrolysed to 8-(3-methoxy-2-*iso*propylphenyl)-5-oxo-octanoic acid (X; R = H, R′ = $CHMe_2$, R″ = OMe) which was converted by the same series of reactions into 1 : 2 : 3 : 4-tetrahydro-7-methoxy-1 : 1-dimethyl-8-*iso*propylphenanthrene (II), identical with the compound A of Short and Wang.[2]

Further studies on the keto-ester (X; R′ = Pr^i, R″ = OMe) and its possible conversion into (±)-totarol by the method described elsewhere [12] are in progress.

Experimental

3-Methoxy-2-isopropylbenzamide.—3-Methoxy-2-*iso*propylbenzonitrile [6] (17·5 g.) was treated with a mixture of 30% hydrogen peroxide (80 ml.), 95% ethanol (120 ml.), and 6N-sodium hydroxide (8 ml.) at 50° for 4 hr. (cf. ref. 7). After neutralisation most of the ethanol was

[10] Ansell and Selleck, *J.*, 1956, 1238.
[11] Robinson and Thompson, *J.*, 1939, 1739.
[12] Nasipuri, *Chem. and Ind.*, 1957, 425.

removed by steam-distillation. On cooling, the heavy oil solidified. On crystallisation from benzene it gave 3-methoxy-2-*iso*propylbenzamide (10 g., 52%), m. p. 126° (Found: C, 68·6; H, 7·8; N, 7·1. Calc. for $C_{11}H_{15}O_2N$: C, 68·4; H, 7·8; N, 7·3%) (Richtzenhain and Nippus [6] give m. p. 124—125°).

3-*Methoxy*-2-iso*propylaniline*.—This amine, b. p. 135°/8 mm., was prepared according to the procedure described in *Organic Reactions* [8] in approximately 70% yield from the preceding amide by the action of 0·5N-sodium hypochlorite at 70°. The *benzoyl derivative* formed needles (from methanol), m. p. 153° (Found: C, 75·4; H, 7·1; N, 5·3. $C_{17}H_{19}O_2N$ requires C, 75·8; H, 7·1; N, 5·2%).

3-*Methoxy*-2-iso*propylphenethyl Alcohol* (VI; R = CH_2·CH_2·OH).—A mixture of 1-iodo-3-methoxy-2-*iso*propylbenzene (27·6 g.) prepared from the above amine by diazotisation, ethyl bromide (10·9 g.), and ether (70 ml.) was added dropwise during 30 min. to a suspension of magnesium (5·2 g.) in ether (30 ml.). Thiophen-free benzene (100 ml.) was next added and the mixture was gently heated under reflux for 2 hr. It was then cooled to 0° and ethylene oxide (10 g.) in ether (50 ml.) was gradually added with stirring and the whole left overnight. Next day the mixture was refluxed for 1 hr., then decomposed with ice and 10% sulphuric acid. The organic layer was separated, washed with water, dried (K_2CO_3), and after removal of the solvent distilled, to give 3-*methoxy*-2-iso*propylphenethyl alcohol* (13·6 g., 70%), b. p. 140—145°/3 mm. (Found: C, 74·3; H, 9·4. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%). Its 3 : 5-*dinitrobenzoate* crystallised from ethanol in light yellow prismatic needles, m. p. 103·5° (Found: C, 58·4; H, 5·2; N, 7·3. $C_{19}H_{20}O_7N_2$ requires C, 58·8; H, 5·2; N, 7·2%). The *bromide* (VI; R = CH_2·CH_2Br), b. p. 135°/3 mm. (Found: C, 56·3; H, 6·8. $C_{12}H_{17}OBr$ requires C, 56·0; H, 6·6%), was prepared [13] from the alcohol by the action of phosphorus tribromide in carbon tetrachloride in 64% yield.

Ethyl α-(3-*Methoxy*-2-iso*propylphenethyl*)-β-*oxopimelate* (VII).—The above bromide (25·7 g.) was added to a cold mixture of ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate (27·2 g.) and ethanolic sodium ethoxide prepared from sodium (2·3 g.) and absolute ethanol (40 ml.), and the whole heated under reflux for 10 hr. The product was worked up in the usual way and on distillation gave the *ester* (VII) (17 g.), b. p. 210—215°/0·1 mm. (Found: C, 68·1; H, 8·6. $C_{23}H_{34}O_6$ requires C, 68·0; H, 8·4%).

γ-(2-*Carboxy*-3 : 4-*dihydro*-6-*methoxy*-5-iso*propyl*-1-*naphthyl*)*butyric Acid* (VIII).—The ester (VII) (5 g.) was treated with concentrated sulphuric acid (15 ml.) at −10° for 3 hr., then poured on ice. The organic matter was taken up in ether and hydrolysed with 5% ethanolic potassium hydroxide to the *acid* (VIII) (3 g., 70%) which crystallised from dilute methanol as prisms, m. p. 195° (Found: C, 68·3; H, 7·0. $C_{19}H_{24}O_5$ requires C, 68·7; H, 7·2%). The *dimethyl ester*, b. p. 210—212°/0·1 mm., (Found: C, 70·1; H, 7·9. $C_{21}H_{28}O_5$ requires C, 70·0; H, 7·8%), was prepared by means of methanol and concentrated sulphuric acid on the steam-bath for 6 hr.

1 : 2 : 3 : 4 : 9 : 10-*Hexahydro*-7-*methoxy*-1-*oxo*-8-iso*propylphenanthrene* (IX).—The preceding ester (3·4 g.) was heated with a suspension of sodium methoxide [from sodium (0·23 g.) and methanol (0·4 ml.)] in dry benzene (6 ml.) for 2 hr. The product was worked up in the usual way and was hydrolysed by refluxing concentrated hydrochloric acid (30 ml.), acetic acid (60 ml.), and water (5 ml.) for 30 min. in nitrogen. The mixture was diluted with water and extracted with ether. The ethereal extract was washed with sodium hydrogen carbonate solution, then with water, dried, and distilled, to give the *ketone* (IX) (1·1 g.), leaflets (from methanol), m. p. 62—63° (Found: C, 80·1; H, 8·3. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·2%). The *dinitrophenylhydrazone* formed red needles (from ethanol), m. p. 225° (Found: C, 64·0; H, 6·0; N, 12·3. $C_{24}H_{26}O_5N_4$ requires C, 64·0; H, 5·8; N, 12·4%).

2-*Methoxy*-8-*methyl*-1-iso*propylphenanthrene* (IV).—A solution of the above ketone (1 g.) in dry benzene (20 ml.) was added at room temperature to a stirred solution of methylmagnesium iodide prepared from magnesium (0·4 g.), methyl iodide (1·2 ml.), and ether (30 ml.). The mixture was refluxed for 4 hr., then decomposed with cold 5% sulphuric acid, and the resultant alcohol was worked up in the usual way and distilled in a high vacuum, to give a semi-solid mass (0·9 g.) which was heated with 30% palladium–charcoal (50 mg.) at 300—310° for 1 hr. (cf. ref. 9). The product (0·5 g.) recovered by means of benzene was chromatographed in light petroleum (b. p. 60—80°) through alumina. Recrystallisation from ethanol gave 2-methoxy-8-methyl-1-*iso*propylphenanthrene (IV) in plates (0·35 g.), m. p. 145° (Found: C, 86·3; H, 7·8. Calc. for $C_{19}H_{20}O$: C, 86·4; H, 7·6%). The picrate separated from ethanol in orange needles,

[13] Hewett, *J.*, 1936, 50.

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m. p. 186—187° (Found: C, 60·8; H, 4·8; N, 8·5. Calc. for $C_{19}H_{20}O,C_6H_3O_7N_3$: C, 60·9; H, 4·7; N, 8·5%). The trinitrobenzene complex formed short needles (from ethanol), m. p. 207—208° (Found: C, 62·9; H, 4·9; N, 8·6. Calc. for $C_{19}H_{20}O,C_6H_3O_6N_3$: C, 62·9; H, 4·8; N, 8·8%). The phenol, m. p. 139—140° (Found: C, 86·6; H, 7·3. Calc. for $C_{18}H_{18}O$: C, 86·4; H, 7·2%), was prepared by boiling the methyl ether (IV) with pyridine hydrochloride. Short and Wang [1] give 144·5—145°, 186—187°, 208—209°, and 139—140° as the respective m. p.s.

1 : 2 : 3 : 4-*Tetrahydro*-1 : 1-*dimethylphenanthrene*.—Methyl γ-1-naphthylbutyrate (7·5 g.) in dry ether (20 ml.) was added dropwise at room temperature to methylmagnesium iodide prepared from magnesium (4 g.), methyl iodide (12 ml.) and ether (60 ml.), and reaction was completed by 2 hours' heating. The complex was decomposed by cold 10% sulphuric acid, and the ethereal layer was washed with water, dried (K_2CO_3), and evaporated at the water-pump. The crude alcohol (XI; R = R′ = H) (8 g.) was cyclised by heating with polyphosphoric acid [prepared from phosphoric oxide (8 g.) and 89% phosphoric acid (40 ml.)] at 160° for 3 hr. with stirring. The product was worked up in the usual way and distilled *in vacuo* over sodium (0·5 g.), to give **1 : 2 : 3 : 4-*tetrahydro*-1 : 1-*dimethylphenanthrene*** (4·8 g., 70%), b. p. 140°/1 mm. (Found: C, 91·5; H, 8·5. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%). The *picrate* crystallised from ethanol in orange-red needles, m. p. 97° (Found: C, 60·3; H, 4·9; N, 9·7. $C_{16}H_{18},C_6H_3O_7N_3$ requires C, 60·1; H, 4·8; N, 9·6%).

***Dehydrogenation of* 1 : 2 : 3 : 4-*Tetrahydro*-1 : 1-*dimethylphenanthrene*.**—The preceding hydrocarbon (1 g.) was heated with powdered selenium (2 g.) for 10 hr. at 300—320°. The product, worked up in the usual way and crystallised from ethanol, gave 1-methylphenanthrene [14] (0·3 g.), m. p. and mixed m. p. 118—119° (picrate, m. p. 135—136°).

γ-6-*Methoxy*-1-*naphthylbutyric Acid*.—Ethyl α-*m*-methoxyphenethyl-β-oxopimelate (35 g.) was refluxed with potassium hydroxide (30 g.) in water (450 ml.) for 10 hr. The cold mixture was extracted with ether, and the alkaline solution was acidified. The organic matter was collected in ether, dried (Na_2SO_4), and after removal of the solvent, distilled, to afford 8-*m*-methoxyphenyl-5-oxo-octanoic acid (X; R = R′ = H, R″ = OMe) (12 g.), b. p. 215—220°/2 mm. The methyl ester was converted by the usual procedure [11] into γ-6-methoxy-1-naphthylbutyric acid, m. p. 149—150°.

1 : 2 : 3 : 4-*Tetrahydro*-7-*methoxy*-1 : 1-*dimethylphenanthrene* (III).—Methyl γ-6-methoxy-1-naphthylbutyrate (3 g.) was treated with excess of methylmagnesium iodide, and the product (3 g.) on cyclodehydration with polyphosphoric acid as before gave **1 : 2 : 3 : 4-tetrahydro-7-methoxy-1 : 1-dimethylphenanthrene** (1·6 g.), b. p. 155—160°/2 mm., which solidified and crystallised from methanol in needles, m. p. 56° (Found: C, 84·9; H, 8·3. Calc. for $C_{17}H_{20}O$: C, 85·0; H, 8·3%). The picrate formed red needles (from ethanol), m. p. 94° (Found: C, 59·0; H, 5·0; N, 8·8. Calc. for $C_{17}H_{20}O,C_6H_3O_7N_3$: C, 58·8; H, 4·9; N, 8·95%). Short and Wang [1] give m. p. 55·5—56° for the methyl ether and m. p. 105—106° (when heated slowly) or 94° (when heated rapidly) for the picrate. We were, however, unable to get the higher m. p. The corresponding phenol crystallised from benzene–light petroleum in needles, m. p. 134° (Found: C, 85·1; H, 8·0. Calc. for $C_{16}H_{16}O$: C, 85·0; H, 8·0%). Short and Wang [1] give m. p. 134—134·5°. The methyl ether (III) (0·7 g.) was dehydrogenated by selenium powder (1·2 g.) at 300—310° for 6 hr. and the product on crystallisation from ethanol (charcoal) gave 7-methoxy-1-methylphenanthrene,[15] m. p. 129—130° (picrate, m. p. 141—142°).

Methyl* 8-(3-*Methoxy*-2-*iso*propylphenyl)-5-*oxo*-*octanoate (X; R = Me, R′ = Pr^i, R″ = OMe).—Ethyl α-(3-methoxy-2-*iso*propylphenethyl)-β-oxopimelate (VII) (12 g.) was heated with potassium hydroxide (7 g.) in water (100 ml.) for 10 hr. and the product was worked up in the usual manner, to give the gummy acid (6 g.). The crude acid was esterified by refluxing methanol (50 ml.) containing 3% hydrochloric acid. The *methyl ester* was obtained as a viscous oil (5 g.), b. p. 187—190°/1 mm. (Found: C, 71·4; H, 8·9. $C_{19}H_{28}O_4$ requires C, 71·3; H, 8·8%).

γ-6-*Methoxy*-5-iso*propyl*-1-*naphthylbutyric Acid*.—The foregoing ester (5 g.) was cyclised by concentrated sulphuric acid (10 ml.) at −10° for 3 hr. The brown mixture was worked up in the usual way, to give **γ-3 : 4-dihydro-6-methoxy-5-*iso*propyl-1-naphthylbutyric acid** (2·7 g.), m. p. 110—115°, which was esterified without further purification. The *methyl ester* (2 g.), b. p. 180—182°/0·1 mm. (Found: C, 75·3; H, 8·9. $C_{19}H_{26}O_3$ requires C, 75·5; H, 8·6%), was dehydrogenated by sulphur (0·22 g.) at 240—250° for 2 hr., and the product hydrolysed by

[14] Haworth, *J.*, 1932, 1125.
[15] Short, Stromberg, and Wiles, *J.*, 1936, 319.

boiling it with potassium hydroxide (1 g.) in 95% ethanol (30 ml.) for 3 hr. The crude *acid* (1·8 g.) was purified by repeated crystallisation from aqueous methanol and formed thick prisms, m. p. 163—164° (Found: C, 75·5; H, 7·8. $C_{18}H_{22}O_3$ requires C, 75·5; H, 7·7%). The *methyl ester* had b. p. 180—182°/0·1 mm. (Found: C, 76·2; H, 8·1. $C_{19}H_{24}O_3$ requires C, 76·0; H, 8·0%).

1 : 2 : 3 : 4-*Tetrahydro*-7-*methoxy*-1 : 1-*dimethyl*-8-iso*propylphenanthrene* (II).—The above ester (1 g.) was treated with excess of methylmagnesium iodide in ether and the resultant alcohol was cyclised as previously described. The product (0·4 g.) was distilled at 0·01 mm. and crystallised from methanol in needles, m. p. 108—109° (0·1 g.) (Found: C, 85·3; H, 9·3. Calc. for $C_{20}H_{26}O$: C, 85·1; H, 9·2%). The trinitrobenzene complex formed orange-red needles (from ethanol), m. p. 150—151° (Found: C, 62·8; H, 5·8; N, 8·3. Calc. for $C_{20}H_{26}O,C_6H_3O_6N_3$: C, 63·0; H, 5·9; N, 8·5%).

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523. *Studies of* Aspergillus Niger. *Part X.* Polyol and Disaccharide Production from Acetate.*

By S. A. BARKER, A. GÓMEZ-SÁNCHEZ, and M. STACEY.

Growth of *A. niger* "152" on acetate as the sole carbon source is shown to produce mannitol, arabitol, erythritol, glycerol, maltose, and αα-trehalose intracellularly. Conditions for the incorporation of [^{14}C]acetate into the polyols and disaccharides are described.

PREVIOUS work[1] has shown that the major carbohydrate component produced intracellularly by *A. niger* "152," grown on sucrose as the sole carbon source, is the linear polyglucosan nigeran. Early attempts[2] to grow this organism on sodium acetate as the sole carbon source were unsuccessful. Recently, however, we have been able to achieve this by heavy inoculation of a 1% sodium acetate medium with mycelia grown on media where the sole source of carbon was D-glucose. Two subsequent subcultures in 4% sodium acetate gave an organism which grew rapidly on 4% sodium acetate and survived in concentrations up to 10% sodium acetate but which was unable to withstand continuous subculturing in 4% sodium acetate. The present communication describes the identification of several polyols and disaccharides produced intracellularly when *A. niger* "152" is grown on 4% sodium acetate.

In all the work described the mineral constituents of the medium were similar to those used by Currie.[3] The mycelia obtained from 20 l. of medium containing sodium acetate (4%) were harvested, washed, and extracted successively with water, 80% ethanol, and 20% ethanol. Cooling the aqueous extract gave no precipitate,[1] indicating that the organism was unable to synthesise nigeran from acetate. A precipitate (A) in the cooled 80% ethanol extract showed none of the properties of nigeran and appeared to be a complex mixture of polysaccharide (galactose, glucose, and probably fructose detected in its hydrolysate) and protein (amino-acids detected on hydrolysis).

The combined extracts were fractionated on a charcoal–Celite column by Whistler and Durso's method.[4] Elution with water gave three fractions (I, II, and III) which, on

* Part IX, *J.*, 1957, 4865.

[1] Barker, Bourne, and Stacey, *J.*, 1953, 3084.
[2] Barker and Carrington, *J.*, 1953, 3588.
[3] Currie, *J. Biol. Chem.*, 1917, **31**, 15.
[4] Whistler and Durso, *J. Amer. Chem. Soc.*, 1950, **72**, 677.

paper chromatography, were found to contain varying proportions of the acyclic polyhydric alcohols, mannitol, arabitol, and erythritol. A further fraction (IV), eluted with aqueous ethanol, appeared to contain maltose and trehalose. Crystalline D-mannitol was obtained from fraction II and was further characterised as its hexa-acetate. Fractionation of the mother-liquors on a cellulose column afforded crystalline erythritol which was further characterised as its di-*O*-benzylidene acetal. Further purification of some of the fractions from the cellulose column by separation on paper chromatograms gave crystalline D-arabitol. Fraction I afforded more di-*O*-benzylidene-erythritol, and fraction III yielded a crop of crystalline mannitol.

Fraction IV was fractionated on a cellulose column and afforded crystalline αα-trehalose dihydrate (further characterised as its octa-acetate) and a fraction which (*a*) showed an infrared spectrum identical with that of maltose and (*b*) gave glucose on treatment with the specific enzyme α-glucamylase.[5]

Two small cultures containing sodium acetate (4%) together with either $CH_3{\cdot}^{14}CO_2Na$ or $^{14}CH_3{\cdot}CO_2Na$ were incubated for 10 days at 30°. Activity determination showed that the highest proportion of labelled carbon was stored in the mycelia grown on $^{14}CH_3{\cdot}CO_2Na$. Radioautography of an extract of each mycelium showed little activity was present in the polyols or disaccharides. A much more efficient method of incorporating the activity was to delay addition of the labelled acetate until 7 days after incubation and then incubate the mixture for a further 3 days. Under these conditions highly active components corresponding to erythritol, arabitol, mannitol, maltose, trehalose, etc., were detected.

One sequence whereby acetate could be incorporated into the polyols would be initiated by its reaction as acetyl coenzyme A in the "glyoxylate cycle." This is the means by which it it believed [6] many moulds can meet all their carbon requirements from acetate. Subsequent conversion of malate, a component of this cycle, into phosphopyruvate, followed by the reversal of the reactions of glycolysis, could then yield hexoses. Hexoses in turn would supply pentoses *via* the pentose phosphate cycle. Present knowledge indicates that the acyclic polyhydric alcohols are synthesised by reduction either of the corresponding ketose phosphate [7] or of the ketose sugars [8] themselves.

Experimental

Growth of Aspergillus niger "152".—Medium (1 l.) was prepared containing NH_4NO_3 (5·0 g.), KH_2PO_4 (2·0 g.), $MgSO_4,7H_2O$ (0·5 g.), $FeSO_4,7H_2O$ (0·05 g.), anhydrous $ZnCl_2$ (0·05 g.), N-HCl (2 c.c.), and glucose (100 g.). After sterilisation by autoclaving at 15 lb./sq. in. for 20 min., the medium was inoculated with *Aspergillus niger* "152" and incubated for 5 days at 30°. Three further batches (each 1 l.) of medium were prepared which contained the mineral constituents mentioned above but in which glucose was replaced by sodium acetate trihydrate (1%; 4%; 4% respectively). Mycelia obtained from the glucose culture were then subcultured successively into these acetate media. Incubation times were 1%, 17 days; 4% (I), 18 days; 4% (II), 8 days and the final pH values of the media 1%, 6·61; 4% (I), 6·0; 4% (II), 7·15. Mycelia from 4% (II) were finally subcultured into twenty 1 l. batches of medium containing sodium acetate trihydrate (4%) and incubated for 7 days at 30°. The mycelia were harvested and then extracted twice with boiling water (1 l.) for 10—15 min. On cooling, no nigeran was deposited. The residual mycelia were extracted successively with boiling 80% ethanol (1 l.) and with boiling 20% ethanol (1 l.). On cooling, the 80% ethanol extract deposited a solid A (0·6 g.). All the extracts were combined, concentrated *in vacuo*, and freeze-dried to a powder B (15·3 g.). Paper chromatography of B in butanol–ethanol–water–ammonia (40 : 10 : 49 : 1) and spraying the chromatogram with a silver nitrate–sodium hydroxide [9] spray revealed

[5] Barker, Bourne, and Fleetwood, *J.*, 1957, 4865.
[6] Kornberg and Krebs, *Nature*, 1957, **179**, 988.
[7] Wolff and Kaplan, *J. Biol. Chem.*, 1956, **218**, 849.
[8] Moore and Rainbow, *J. Gen. Microbiol.*, 1955, **13**, 190.
[9] Trevelyan, Proctor, and Harrison, *Nature*, 1950, **166**, 444.

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components with the same mobilities as maltose, mannitol (or glucose), arabitol, erythritol, and glycerol together with another component of R_G 0·75.

Fractionation of B. Fraction B was dissolved in water (100 c.c.) and fractionated on a charcoal–Celite column (l 65 cm., diam. 4·5 cm.) by Whistler and Durso's method.[4] Elution with water gave fraction I, 5·01 g.; fraction II, 3·15 g.; and fraction III, 1·06 g. Further elution with increasing concentrations of aqueous ethanol gave fraction IV, 0·248 g.

Fraction I was extracted with boiling methanol (3 × 100 c.c.; 1 × 50 c.c.), and the extracts were concentrated to a syrup (1·3 g.). A portion (0·1 g.) crystallised from aqueous ethanol, to give an unknown product, m. p. 326—328°, which on combustion left a residue (21·6%) and was not further investigated. The mother-liquors were concentrated to a syrup and treated with benzaldehyde (3·5 c.c.) and concentrated hydrochloric acid (4 c.c.) at room temperature for 3 days. The mixture was then poured into water and extracted with ether (3 × 10 c.c.), and the extract washed with aqueous sodium hydrogen carbonate (2 × 5 c.c.), then sodium hydrogen sulphite (3 × 10 c.c.), dried (Na_2SO_4), and evaporated. The residue crystallised from ethanol and after recrystallisation gave needles, m. p. 194—196° (Jayme and Maris [10] give 197° for dibenzylidene-erythritol).

Fraction II left a small residue (0·12 g.) on extraction with boiling methanol (100 c.c.). On cooling, the methanol extract deposited crystals (0·79 g.) which after several recrystallisations from methanol–water gave D-mannitol (0·45 g.), m. p. and mixed m. p. 164·5—166° (Found: C, 39·7; H, 7·7. Calc. for $C_6H_{14}O_6$: C, 39·6; H, 7·7%). Acetylation with sodium acetate–acetic anhydride gave mannitol hexa-acetate, m. p. 123—124° (Found: C, 49·8; H, 6·0. Calc. for $C_{18}H_{26}O_{12}$: C, 49·8; H, 6·0%).

The mother-liquors from the crystallisation of mannitol were evaporated to a syrup (2 g.), and a part (1 g.) was fractionated on a cellulose column washed with the organic phase of butanol–ethanol–water–ammonia (40 : 10 : 49 : 1). After analysis of the fractions collected, all those containing erythritol were concentrated to a syrup (0·37 g.). Crystallisation from ethanol afforded *meso*-erythritol, m. p. and mixed m. p. 118—119° (Found: C, 39·6; H, 8·5. Calc. for $C_4H_{10}O_4$: C, 39·35; H, 8·3%). Treatment of a portion (0·05 g.) with benzaldehyde (0·2 c.c.) and concentrated hydrochloric acid (0·25 c.c.) (as above) gave dibenzylidene-erythritol, m. p. 200—201°. The remaining fractions (0·61 g.) were refractionated twice on a cellulose column without affording pure arabitol. A part (38 mg.) was therefore separated on sheets of Whatman No. 1 paper, the bands containing the arabitol being eluted and freeze-dried (32 mg.). Crystallisation from aqueous ethanol gave D-arabitol, m. p. and mixed m. p. 104—105°. Its infrared spectrum (700—3000 cm.$^{-1}$) was also identical with that of D-arabitol.

Fraction III, on paper chromatography, was shown to contain more arabitol and mannitol.

Fraction IV on paper chromatographic and ionophoretic examination showed two components with the mobilities of maltose and trehalose. Separation on a cellulose column (as above) gave one fraction (14 mg.) containing maltose and another (120 mg.) containing trehalose. The maltose fraction was characterised by (*a*) its infrared spectrum which was identical with that of an authentic specimen and (*b*) incubation of a portion (5 mg.) with α-glucamylase (10 mg.) at 30°, whereafter glucose could be detected (30 min.) and all the maltose was hydrolysed (12 hr.). The trehalose fraction crystallised from aqueous ethanol, to give αα-trehalose dihydrate (0·09 g.), m. p. and mixed m. p. 96—98°. Treatment of a portion (50 mg.) with sodium acetate (50 mg.) and acetic anhydride (0·5 c.c.) gave trehalose octa-acetate, m. p. 97—98° (Hudson and Johnson [11] give 96—98°) (Found: C, 49·3; H, 5·8. Calc. for $C_{28}H_{38}O_{19}$: C, 49·6; H, 5·6%).

Examination of A. Material A was insoluble in boiling water and in cold N-sodium hydroxide. Hydrolysis of a portion (20 mg.) with 2N-sulphuric acid at 100° for 3—4 hr. gave, *inter alia*, glucose, fructose, galactose, and amino-acids when examined paper chromatographically.

Incorporation of [^{14}C]Acetate into the Polyols and Disaccharides.—(*a*) Mineral medium (5 c.c.; composed as above) containing sodium acetate trihydrate (4%) and $CH_3{\cdot}^{14}CO_2Na$ (0·8 mg.; 50 μc) was sterilised and then inoculated with *A. niger* " 152 " from the 4% acetate (I) culture described above. After incubation for 10 days, the mycelia produced were filtered off, washed with water, and freeze-dried (1·6 mg.). When spread on an aluminium disc, these mycelia showed an activity of 1647 counts per min. per mg. in position 3 of a counter. The mycelia were

[10] Jayme and Maris, *Ber.*, 1944, **77**, 383.
[11] Hudson and Johnson, *J. Amer. Chem. Soc.*, 1915, **37**, 2748.

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extracted with boiling water (2 × 2 c.c.), 80% ethanol (2 × 2 c.c.), and 20% ethanol (2 × 2 c.c.), and the material deposited from the 80% ethanol extract removed by centrifugation. The mixed extracts were concentrated to 0·5 c.c. Portions (50 μl.; 125 μl.) with activities 800 c/min. and 2000 c/min. respectively were separated on Whatman No. 1 paper irrigated with the organic phase of butanol–ethanol–water–ammonia (40 : 10 : 49 : 1) for 3 days. After exposure to *X*-ray film for 15 days no mobile components could be detected in the smaller portion, and only maltose and trehalose could be detected weakly in the larger. In both portions most of the radioactivity remained on the base line.

The above procedure was repeated with $^{14}CH_3 \cdot CO_2Na$ (1·0 mg.; 25 μc). The mycelia obtained (2·5 mg.) had 2611 counts per min. per mg. in position 3 of the counter. A portion (50 μl.; 1000 c/min.), when analysed on a chromatogram as above, showed weakly active components corresponding to maltose and trehalose.

(*b*) Mineral medium (5 c.c.) containing sodium acetate trihydrate (4%) was sterilised and inoculated in the usual manner. After incubation for 7 days, $CH_3 \cdot {}^{14}CO_2Na$ (1·0 mg.; 63 μc) in sterile water (1 c.c.) was added and the culture incubated for a further 3 days. The mycelia obtained (6 mg.) showed 1320 counts per min. per mg. in position 4 of the counter and were extracted as above. A portion (150 μl.; 21,000 c/min.) of the extract was analysed by paper chromatography and radioautography (exposure time, 7 days). Strongly active components corresponding to maltose, trehalose, mannitol, arabitol, and two unknown components were detected together with a weakly active component corresponding to erythritol.

A similar experiment was carried out involving addition of $^{14}CH_3 \cdot CO_2Na$ (0·975 mg.; 25 μc) in sterile water (0·5 c.c.) to a 4% sodium acetate culture (5·25 c.c.) after incubation for 7 days. After further incubation for 3 days, radioautography of an extract of the mycelia (3 mg.) again showed strongly active polyols and disaccharides.

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524. *Sugar Nitrates. Part V.* Removal of Nitrate Groups.*

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Sugar nitrates are completely converted into the alcohols by excess of hydrazine hydrate in boiling ethanol. In this way a nitrate group is removed selectively from a compound also containing toluene-*p*-sulphonate, methanesulphonate, methyl, or benzyl groups. Treatment of D-glucose 2 : 3-dinitrates with one mol. of hydrazine hydrate gives equal amounts of the two mononitrates, making D-glucose 2-nitrates more readily available.

*cyclo*Hexyl nitrate with sodium iodide in methanol gives sodium nitrate and *cyclo*hexene. *trans-cyclo*Hexane-1 : 2-diol dinitrate and 1 : 3-*O*-benzylideneglycerol 2-nitrate are resistant to reaction with sodium iodide, but small amounts of the alcohols are produced. Sodium iodide in acetone with 1 : 3-2 : 4-di-*O*-ethylidenesorbitol 5 : 6-dinitrate gives 5 : 6-didehydro-5 : 6-dideoxy-1 : 3-2 : 4-di-*O*-ethylidenesorbitol (mainly) and 1 : 3-2 : 4-di-*O*-ethylidenesorbitol 6-nitrate, the latter also being obtained by reaction of the 5 : 6-dinitrate with sodium nitrite in aqueous ethanol.

cis- and *trans-cyclo*Hexane-1 : 2-diol dinitrates with cold concentrated sulphuric acid yield the corresponding di(hydrogen sulphates).

HYDRAZINE HYDRATE is an excellent reagent for reducing sugar nitrates.[1] In contrast to the complex reaction of the nitrates of primary aliphatic alcohols,[2] sugar nitrates are reduced by hydrazine, even in aqueous ethanol, with formation of the alcohol only. The procedure is similar to that for the reduction of aromatic nitro-compounds with hydrazine

* Part IV, *J.*, 1958, 537.

[1] Ennor, Honeyman, and Stening, *Chem. and Ind.*, 1956, 1308.
[2] Merrow and Van Dolah, *J. Amer. Chem. Soc.*, 1954, **76**, 4522.

hydrate in the presence of Raney nickel,[3] palladium–charcoal,[4] or copper or iron powder,[5] but for sugar nitrates a catalyst is generally unnecessary. The method enables a nitrate group to be removed selectively from a compound also containing toluene-*p*-sulphonate, methanesulphonate, methyl, or benzyl groups.

The 2 : 3-dinitrates of methyl 4 : 6-*O*-ethylidene-α-D-glucoside and its anomer, and of methyl 4 : 6-*O*-benzylidene-α-D-glucoside are partially reduced when boiled in ethanol for 3·5 hours with 1·2 moles of hydrazine hydrate per mole of dinitrate. From each dinitrate, equal amounts of the two mononitrates and a little starting compound were obtained. Thus the reaction proceeds equally readily for each nitrate group and is independent of the nature of the 4 : 6-acetal grouping and of the configuration of the methyl group. This method makes such 2-nitrates available for the first time, although a low yield of methyl 4 : 6-*O*-benzylidene-α-D-glucoside 2-nitrate has been obtained through migration of the nitrate group from $C_{(3)}$ to $C_{(2)}$.[6] Proof that migration of nitrate does not occur during the reactions with hydrazine was obtained by boiling methyl 4 : 6-*O*-ethylidene-α-D-glucoside 3-nitrate with an equimolecular proportion of hydrazine hydrate in ethanol for 3 hours: unchanged starting compound (31%) and methyl 4 : 6-*O*-ethylidene-α-D-glucoside (43%) (but no 2-nitrate) were isolated. The reaction of methyl 4 : 6-*O*-ethylidene-α-D-glucoside 2-nitrate was similar.

Sugar acetates, benzoates, and benzenesulphinates, esterified on primary or secondary alcoholic groups, are converted into the alcohols on being boiled with hydrazine hydrate in ethanol for 90 minutes. Methyl 4 : 6-*O*-benzylidene-α-D-glucoside was obtained from its 2 : 3-diacetate, and acetamide and 1 : 2-3 : 5-di-*O*-methylene-D-glucose from the 6-acetate. This shows that fission of the oxygen–carbon bond takes place during deacetylation. Benzoyl groups are removed more slowly; for example, after 90 minutes' boiling, 1 : 2-5 : 6-di-*O*-*cyclo*hexylidene-D-glucose 3-benzoate was recovered (52%) together with 1 : 2-5 : 6-di-*O*-*cyclo*hexylidene-D-glucose (31%) and benzamide (14%). After 14 hours' boiling, the products were starting compound (1%), 1 : 2-5 : 6-di-*O*-*cyclo*hexylidene-D-glucose (90%), benzamide (7%), and benzhydrazide (33%). The benzhydrazide may have been formed by reaction of benzamide with excess of hydrazine, a reaction which is known to occur in aqueous solution.[7] Analogous products were obtained from 1 : 2-5 : 6-di-*O*-*iso*propylidene-D-glucose 3-benzoate, and methyl 4 : 6-*O*-benzylidene-α-D-glucoside was obtained from its 2 : 3-dibenzoate and from its 2 : 3-dibenzenesulphinate. This is another example of sulphinates' reacting in the manner of carboxylic esters and unlike sulphonates.[6]

Kuhn [8] achieved quantitative reduction of sugar nitrates at room temperature by catalytic hydrogenation under pressure with palladium–charcoal. These reactions have now been found to proceed smoothly at atmospheric pressure.

In Part II [6] a possible mechanism was suggested to explain the replacement by hydroxyl of a nitrate group on a secondary carbon atom in a sugar on reaction with sodium iodide in methanol. However, a fully substantiated reaction sequence was not presented. To try to rectify this, it was considered desirable to study a simple compound having a nitrate group on a secondary carbon atom which, when treated with sodium iodide in methanol, would give the corresponding alcohol. *cyclo*Hexyl nitrate is the simplest compound having a nitrate group on a secondary carbon atom which forms part of a six-membered ring. This nitrate with sodium iodide in methanol at 100° during 66 hours gave *cyclo*hexene, sodium nitrate (in nearly quantitative yield), and a little iodine, but no inorganic nitrite. This reaction is therefore not analogous to those of secondary sugar nitrates, which invariably yield the alcohol, free iodine, and inorganic nitrite. It is noteworthy that *cyclo*hexyl

[3] Balcom and Furst, *J. Amer. Chem. Soc.*, 1953, **75**, 4334; Furst and Moore, *ibid.*, 1957, **79**, 5492.
[4] Dewar and Mole, *J.*, 1956, 2556.
[5] Kubota, Nara, and Onishi, *J. Pharm. Soc. Japan*, 1956, **76**, 801.
[6] Honeyman and Morgan, *J.*, 1955, 3660.
[7] Curtius and Struve, *J. prakt. Chem.*, 1894, **50**, 295.
[8] Kuhn, *J. Amer. Chem. Soc.*, 1946, **68**, 1761.

nitrate decomposes on distillation into *cyclo*hexene and nitric acid.[9] The structure of 1 : 3-*O*-benzylideneglycerol 2-nitrate is more like those of pyranose sugar nitrates. This compound reacted very slowly with sodium iodide in methanol at 100° and after 44 hours was unchanged apart from formation of a little 1 : 3-*O*-benzylideneglycerol, sodium nitrite, and iodine. *trans-cyclo*Hexane-1 : 2-diol dinitrate has been found to be very resistant to reaction with sodium iodide: after its solution in *n*-propyl alcohol had been boiled for 5 days, unchanged starting compound was recovered, together with only a small quantity of the diol. Thus these reactions, although analogous to those of secondary sugar nitrates, are too slow to permit detailed kinetic studies.

Bladon and Owen [10] found that 1 : 3-2 : 4-di-*O*-ethylidenesorbitol 5 : 6-ditoluene-*p*-sulphonate reacted readily with sodium iodide in acetone at 100°, to yield 5 : 6-didehydro-5 : 6-dideoxy-1 : 3-2 : 4-di-*O*-ethylidenesorbitol. The corresponding 5 : 6-dinitrate has now been heated with sodium iodide in acetone at 100° for 2 hours, 5 : 6-didehydro-5 : 6-dideoxy-1 : 3-2 : 4-di-*O*-ethylidenesorbitol (14%), 1 : 3-2 : 4-di-*O*-ethylidenesorbitol 6-nitrate (12%), and unchanged starting compound being obtained; after 21 hours' reaction, the products were the dehydro-compound (51%) and the 6-nitrate (8%). This is the first instance of the formation of an ethylenic compound from a sugar nitrate. The first stage in the formation of the unsaturated compound is probably the replacement, by iodine, of the nitrate group on the primary carbon atom. Although chromatography was used for separating the products, no 6-deoxy-6-iodo-1 : 3-2 : 4-di-*O*-ethylidenesorbitol 5-nitrate was isolated, suggesting that if formed it was rapidly converted into the unsaturated compound. Bladon and Owen [10] postulated intermediate formation of an unstable vicinal di-iodide in the reaction of ditoluene-*p*-sulphonates of 1 : 2-glycols with sodium iodide, leading to unsaturated products. However, a similar mechanism is unlikely to hold for the reaction of the nitrates because in all known examples nitrate groups on secondary carbon atoms are replaced by hydroxyl and not by iodine. Probably, 6-deoxy-6-iodo-1 : 3-2 : 4-di-*O*-ethylidenesorbitol 5-nitrate yields the unsaturated compound directly by a mechanism analogous to that proposed by Foster and Overend [11] for terminal vicinal ditoluene-*p*-sulphonates.

Sodium nitrite in aqueous ethanol reacted slowly with the dinitrate of *trans-cyclo*hexane-1 : 2-diol; after 6 days' boiling the dinitrate was mainly unchanged, apart from a little which had been converted into the *trans*-diol. The 5-nitrate group of 1 : 3-2 : 4-di-*O*-ethylidenesorbitol 5 : 6-dinitrate was removed slowly but selectively by this reagent. As with 1 : 2-3 : 4-di-*O*-*iso*propylidene-D-galactose 6-nitrate,[1] the nitrate group on the primary carbon atom resists attack, confirming the view that the reaction of sodium nitrite is fundamentally different from that of sodium iodide.

Qualitative tests show that when a compound containing a nitrate group is stirred with cold concentrated sulphuric acid nitric acid is liberated. This is detectable with diphenylamine [12] or *NN'*-diphenylbenzidine,[13] each of which gives an intense blue colour. The possible use of concentrated sulphuric acid for removing nitrate groups was investigated in the cases of *cis*- and *trans-cyclo*hexane-1 : 2-diol dinitrate. After treatment of these esters with cold concentrated sulphuric acid during 10 minutes the di(hydrogen sulphates) of the diols were isolated as their barium and bisphenylhydrazine salts. The assigned configurations were confirmed by hydrolysing the di(hydrogen sulphates) to the respective diols. The same esters were obtained directly by treating the diols with concentrated sulphuric acid. Esters which display complex ionisation in sulphuric acid are not regenerated when the solution is poured into water.[14] Thus *cis*- and *trans-cyclo*hexane-1 : 2-diol dinitrate probably undergo complex ionisation in sulphuric acid, similar to that suggested by Kuhn [15]

[9] Fichter and Petrovitch, *Helv. Chim. Acta*, 1941, **24**, 253.
[10] Bladon and Owen, *J.*, 1950, 598.
[11] Foster and Overend, *J.*, 1951, 3452.
[12] Oldham, *J.*, 1925, 2840.
[13] Dewar and Fort, *J.*, 1944, 492.
[14] Hammett and Treffers, *J. Amer. Chem. Soc.*, 1937, **59**, 1708.
[15] Kuhn, *ibid.*, 1947, **69**, 1974.

for ethyl nitrate on the basis of cryoscopic and spectroscopic evidence. Hydrolysis did not occur when the sulphuric acid solution was poured into water, for the *trans*-dinitrate is not decomposed by aqueous sulphuric acid.

Experimental

Unless stated, solutions in benzene or chloroform were dried over anhydrous sodium sulphate, evaporations were conducted under reduced pressure, specific rotations were determined in dry chloroform, and the light petroleum used had b. p. 60—80°.

Chromatographic separations were carried out with columns of activated alumina, Type H, 100/200 S mesh, supplied by Messrs. Peter Spence & Sons, Ltd.

100% Hydrazine hydrate was used.

At the end of the time specified for the preparation of esters in pyridine a little water was added to decompose excess of acid chloride, and the solution was left for 30 min. before it was poured into water.

Where appropriate, identity was established by mixed m. p. and infrared spectra.

Analytical Procedures.—The presence of nitrite ion was established by the appearance of a red colour after the addition of a solution of sulphanilic acid in acetic acid, followed by a solution of α-naphthylamine.

Sodium nitrate in the absence of nitrite was detected by fusion of the solid to give nitrite which liberated iodine from acidified aqueous potassium iodide. Nitrate was determined quantitatively by reduction to ammonia with Devarda's alloy.

Preparation of Nitrates.—Fuming nitric acid (*d* 1·50; 4·8 ml.) in acetic anhydride (12 ml.) was added slowly to methyl 4 : 6-*O*-benzylidene-α-D-mannoside [15] (6·0 g.) suspended in acetic anhydride (12 ml.) at 0°. After 10 min. at room temperature, the resulting solution was poured into iced aqueous potassium carbonate. After being washed with dilute aqueous potassium carbonate and then with water and dried, the crystalline product (7·0 g., 88%) was recrystallised from methanol, to yield *methyl* 4 : 6-O-*benzylidene*-α-D-*mannoside* 2 : 3-*dinitrate* (5·46 g., 69%), m. p. 142°, $[\alpha]_D^{20}$ −3·1° (*c* 2·4) (Found: C, 45·4; H, 4·5; N, 7·4. $C_{14}H_{16}O_{10}N_2$ requires C, 45·2; H, 4·3; N, 7·5%).

Unless otherwise stated, this procedure was employed in the succeeding experiments. The product obtained from 1 : 3-2 : 4-di-*O*-ethylidenesorbitol was recrystallised from ethanol–light petroleum or aqueous ethanol, to yield cubes of 1 : 3-2 : 4-*di*-O-*ethylidenesorbitol* 5 : 6-*dinitrate* (70%), m. p. 80—80·5°, $[\alpha]_D^{26}$ +8·7° (*c* 3·4) (Found: C, 37·4; H, 4·9; N, 8·3. $C_{10}H_{16}O_{10}N_2$ requires C, 37·0; H, 4·9; N, 8·6%).

The crude precipitate obtained from 1 : 3-*O*-benzylideneglycerol was recrystallised from methanol to give needles of 1 : 3-*O*-*benzylideneglycerol* 2-*nitrate* (27%), m. p. 93—93·5° (Found: C, 53·5; H, 5·1; N, 6·1. $C_{10}H_{11}O_5N$ requires C, 53·3; H, 4·9; N, 6·2%).

A solution of the viscous product obtained from *trans-cyclo*hexane-1 : 2-diol was dissolved in ether and washed with aqueous sodium hydrogen carbonate and then with water near 0°. Evaporation of the dried ether solution yielded a liquid which was chromatographed. Elution by light petroleum afforded *trans-cyclo*hexane-1 : 2-diol dinitrate (67%), n_D^{20} 1·4754, m. p. 17·5—18°. Christian and Purves [17] record m. p. 18·5—19°.

The same procedure was followed with the *cis*-isomer except that elution with benzene yielded *cis-cyclo*hexane-1 : 2-diol dinitrate (64%), m. p. 22—23°, which, after one recrystallistion from light petroleum, had m. p. 24°, n_D^{20} 1·4772. Christian and Purves [17] record m. p. 24·5—25°, n_D^{21} 1·4790.

In the case of *cyclo*hexanol, the reaction solution was left at 0° overnight. The oily product, dissolved in light petroleum, was repeatedly washed with aqueous sodium hydrogen carbonate and then with water until the aqueous extract was neutral. The dried petroleum solution was evaporated and the residue was distilled to yield *cyclo*hexyl nitrate (74%), b. p. 56—58°/7 mm., middle fraction, b. p. 56°/7 mm., n_D^{20} 1·4546, d_{16}^{16} 1·104 (Found: N, 9·6. Calc. for $C_6H_{11}O_3N$: N, 9·65%). Kornblum and Teitelbaum [18] record n_D^{20} 1·4562, d_4^{20} 1·1043.

Reduction of Sugar Nitrates with Hydrazine Hydrate.—A solution of methyl 4 : 6-*O*-benzylidene-α-D-glucoside 2 : 3-dinitrate (1·49 g., 1 mol.) and hydrazine hydrate (1·20 g., 6 mol.) in

[15] Schwarz, unpublished results.
[17] Christian and Purves, *Canad. J. Chem.*, 1951, **29**, 926.
[18] Kornblum and Teitelbaum, *J. Amer. Chem. Soc.*, 1952, **74**, 3078.

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ethanol (15 ml.) was boiled under reflux for 90 min. Excess of hydrazine was then decomposed by boiling the solution with Raney nickel for 15 min. The solution, after being filtered, was evaporated to a solid which, recrystallised from chloroform–light petroleum, was methyl 4 : 6-*O*-benzylidene-α-D-glucoside (0·90 g., 80%), m. p. 164—165°.

In succeeding experiments, unless otherwise stated, this procedure was used, except that chloroform was added when the compound was insufficiently soluble in boiling ethanol.

Repetition of the above experiment but without addition of nickel led to the same product (74%).

The results are summarised in the annexed Table.

Compound reduced	Yield (%) of alcohol	M. p.	$[\alpha]_D^{20}$
1 : 2-5 : 6-Di-*O*-*cyclo*hexylidene-D-glucose 3-nitrate	90	133—134°	+1·1°
1 : 2-3 : 4-Di-*O*-*iso*propylidene-D-galactose 6-nitrate	100	Liquid *	−57·3
Methyl 4 : 6-*O*-benzylidene-α-D-mannoside 2 : 3-dinitrate ...	84	142—143	+63·5
Methyl 4 : 6-*O*-benzylidene-α-D-altroside 2 : 3-dinitrate	74	170	+116
Methyl 4 : 6-*O*-benzylidene-α-D-altroside 3-nitrate	98	169—170	+115
1 : 3-2 : 4-Di-*O*-ethylidenesorbitol 5 : 6-dinitrate	75	212—213	−11·5 (H_2O)

* Identified as the 6-toluene-*p*-sulphonate, m. p. 90—91°.

Partial Reduction of 2 : 3-*Dinitrates with Hydrazine.*—A solution of methyl 4 : 6-*O*-ethylidene-α-D-glucoside 2 : 3-dinitrate (6·20 g., 1 mol.) and hydrazine hydrate (1·2 g., 1·2 mol.) in ethanol (30 ml.) was boiled under reflux for 3·5 hr., then evaporated, and the residue was chromatographed in benzene. Elution with this solvent and recrystallisation from light petroleum yielded unchanged starting compound (0·28 g., 4·5%), m. p. 100—101°. Elution with ether removed, in the early fractions, a solid which recrystallised from ethanol–light petroleum in long needles of *methyl* 4 : 6-O-*ethylidene*-α-D-*glucoside* 2-*nitrate* (1·81 g., 34%), m. p. 133°, $[\alpha]_D^{17\cdot5}$ +147° (*c* 1·1) (Found: C, 40·8; H, 5·6; N, 4·9%). Further elution with ether and finally with chloroform yielded a solid which, recrystallised from ethanol–light petroleum, was the 3-nitrate (1·82 g., 34%), m. p. 173—174°. No product was eluted by ethanol.

By similar reactions, methyl 4 : 6-*O*-ethylidene-β-D-glucoside 2 : 3-dinitrate gave the 2-*nitrate* (22%), m. p. 144°, $[\alpha]_D^{20}$ −43·8° (*c* 1·0) (Found: C, 40·9; H, 5·7; N, 5·0. $C_9H_{15}O_8N$ requires C, 40·8; H, 5·7; N, 5·3%), the 3-nitrate (24%), and unchanged starting compound (3%), whereas methyl 4 : 6-*O*-benzylidene-α-D-glucoside 2 : 3-dinitrate yielded starting compound (8%), the 2-nitrate (30%), and the 3-nitrate (28%).

Characterisation of the 2-*Nitrates.*—Silver oxide (2 g.) was added in portions to a suspension of methyl 4 : 6-*O*-ethylidene-α-D-glucoside 2-nitrate (0·70 g.) in boiling methyl iodide (6 ml.). The mixture was boiled for 8 hr. before the silver residue was filtered off and washed with chloroform, and the combined filtrate and washings were evaporated. The crystalline residue (0·71 g., 96%), m. p. 86—87°, recrystallised from methanol, gave prisms of *methyl* 4 : 6-O-*ethylidene*-3-O-*methyl*-α-D-*glucoside* 2-*nitrate*, m. p. 87—87·5°, $[\alpha]_D^{20}$ +147° (*c* 0·8) (Found: C, 42·8; H, 6·1. $C_{10}H_{17}O_8N$ requires C, 43·0; H, 6·1%). A solution of this compound (0·70 g.) and hydrazine hydrate (0·37 g.) in ethanol (7 ml.) was boiled under reflux for 1·5 hr. The product, recrystallised from chloroform–light petroleum, was methyl 4 : 6-*O*-ethylidene-3-*O*-methyl-α-D-glucoside (0·45 g., 76%), m. p. 106°, $[\alpha]_D^{21}$ +146° (*c* 1·3) (Found: C, 51·2; H, 7·7. Calc. for $C_{10}H_{18}O_6$: C, 51·3; H, 7·7%). Jeanloz and Gut [19] record m. p. 106—107°, $[\alpha]_D^{21}$ +150° ± 5°. A solution of this compound (0·14 g.) in aqueous N-sulphuric acid (10 ml.) was heated at 100° for 6 hr. The solution was neutralised with barium carbonate and filtered, and the filtrate was evaporated to a syrup which solidified after repeated evaporation of its solutions in ethanol. Recrystallisation from ethanol yielded 3-*O*-methyl-α-D-glucose [20] (0·06 g., 51%), m. p. 158—160°.

Methylation of methyl 4 : 6-*O*-ethylidene-β-D-glucoside 2-nitrate yielded a solid (95%), m. p. 81·5—82·5°, which recrystallised from light petroleum in prisms of *methyl* 4 : 6-O-*ethylidene*-3-O-*methyl*-β-D-*glucoside* 2-*nitrate*, m. p. 83—84°, $[\alpha]_D^{20}$ −22° (*c* 0·5) (Found: C, 42·7; H, 6·0%). Reaction of this compound with hydrazine hydrate yielded a solid which, recrystallised from chloroform–light petroleum, was methyl 4 : 6-*O*-ethylidene-3-*O*-methyl-β-D-glucoside (75%) m. p. 133—134°. Dewar and Fort [13] record m. p. 134°.

Methylation of methyl 4 : 6-*O*-benzylidene-α-glucoside 2-nitrate yielded a solid (98%),

[19] Jeanloz and Gut, *J. Amer. Chem. Soc.*, 1954, **76**, 5793.
[20] Glen, Myers, and Grant, *J.*, 1951, 2568.

m. p. 149—150°, which recrystallised from methanol in needles of *methyl* 4 : 6-O-*benzylidene*-3-O-*methyl*-α-D-*glucoside* 2-*nitrate*, m. p. 149—150°, $[\alpha]_D^{20}$ +102° (*c* 1·1) (Found: C, 53·1; H, 5·6. $C_{15}H_{19}O_8N$ requires C, 52·8; H, 5·6%). Reduction of this with hydrazine hydrate yielded a solid which, recrystallised from ethanol, was methyl 4 : 6-*O*-benzylidene-3-*O*-methyl-α-D-glucoside (70%), $[\alpha]_D^{20}$ +118° (*c* 1·1 in $CHCl_3$·$CHCl_3$), m. p. 146°, undepressed on admixture with a sample prepared in the following experiment. Bolliger and Prins [11] record m. p. 150—151°, $[\alpha]_D^{14}$ +119·5° (in $CHCl_3$·$CHCl_3$) for this compound.

Methanol (2 ml.) containing sodium (50 mg.) and methyl 4 : 6-*O*-benzylidene-3-*O*-methyl-α-D-glucoside 2-toluene-*p*-sulphonate (70 mg.) was boiled under reflux for 8 hr. The cooled solution was neutralised with acetic acid and then evaporated. The residual solid was shaken with warm benzene, and this extract was chromatographed. Elution with benzene removed impurities but washing the column with chloroform afforded a solid which, recrystallised from ethanol–light petroleum, was methyl 4 : 6-*O*-benzylidene-3-*O*-methyl-α-D-glucoside (29 mg., 63%), m. p. 146—147°, $[\alpha]_D^{18}$ +117° (*c* 1·0 in $CHCl_3$·$CHCl_3$).

Reduction of Methyl 4 : 6-O-*Ethylidene*-α-D-*glucoside* 3-*Nitrate and* 2-*Nitrate*.—A solution of the 3-nitrate (0·795 g., 1 mol.) and hydrazine hydrate (0·15 g., 1 mol.) in ethanol (7 ml.) was boiled under reflux for 3 hr. Evaporation yielded a solid which was chromatographed in chloroform solution. Elution with chloroform yielded starting compound (0·25 g., 31%) which after being recrystallised from ethanol–light petroleum had m. p. 175—176°. Ethanol eluted a solid which, recrystallised from ether, was methyl 4 : 6-*O*-ethylidene-α-D-glucoside (0·28 g., 43%), m. p. 75—76°.

Similar reaction with the 2-nitrate yielded unchanged starting compound (25%) and methyl 4 : 6-*O*-ethylidene-α-D-glucoside (47%).

Preparation of Methyl 4 : 6-O-*Ethylidene*-α-D-*glucoside Mononitrate Monotoluene*-p-*sulphonates*.—Toluene-*p*-sulphonyl chloride (0·46 g.) in pyridine (0·5 ml.) was added to a solution of the 3-nitrate (0·53 g.) in pyridine (0·7 ml.) at 0°. After 23 hr. at room temperature, the mixture was poured into ice-water, and the resulting solid was recrystallised from ethanol giving needles of *methyl* 4 : 6-O-*ethylidene*-α-D-*glucoside* 3-*nitrate* 2-*toluene*-p-*sulphonate* (0·66 g., 79%), m. p. 134—134·5°, $[\alpha]_D^{22}$ +104° (*c* 1·0) (Found: C, 46·1; H, 4·8. $C_{16}H_{21}O_{10}NS$ requires C, 45·8; H, 5·0%).

Similarly the 2-nitrate was converted into cubes of *methyl* 4 : 6-O-*ethylidene*-α-D-*glucoside* 2-*nitrate* 3-*toluene*-p-*sulphonate* (55%), m. p. 152—153°, $[\alpha]_D^{20}$ +96·3° (*c* 1·2) (Found: C, 45·9; H, 5·0%).

Selective Removal of Nitrate Groups with Hydrazine Hydrate.—The compounds which were recovered unchanged after being boiled with hydrazine hydrate in ethanol during 1·5 hr. in the presence or absence of Raney nickel included methyl 4 : 6-*O*-benzylidene-α-D-glucoside ditoluene-*p*-sulphonate (88%), dimethanesulphonate (86%), dimethyl ether (88%), and dibenzyl ether (94%), 1 : 2-3 : 4-di-*O*-*iso*propylidene-D-galactose 6-toluene-*p*-sulphonate (81%), and methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene-α-D-alloside (89%).

Selective removal of the nitrate group from the mononitrate of each of the following compounds was achieved under the standard conditions described above: methyl 4 : 6-*O*-benzylidene-α-D-glucoside 3-toluene-*p*-sulphonate (71%), m. p. 159—160°, 2-toluene-*p*-sulphonate (74%), m. p. 153·5—154°, $[\alpha]_D^{21}$ +62·9° (*c* 1·3), 2-methanesulphonate (70%), m. p. 131·5—132°, $[\alpha]_D^{23}$ +72° (*c* 1·1), 3-methanesulphonate (87%), m. p. 142—143°, $[\alpha]_D^{24}$ +88° (*c* 1·0), clustered needles (from chloroform–light petroleum) of *methyl* 4 : 6-O-*ethylidene*-α-D-*glucoside* 2-*toluene*-p-*sulphonate* (88%), m. p. 150°, $[\alpha]_D^{22}$ +82·1° (*c* 1·2) (Found: C, 51·6; H, 5·9; S, 8·3. $C_{16}H_{22}O_8S$ requires C, 51·3; H, 5·9; S, 8·6%), and the 3-*toluene*-p-*sulphonate* (69%), m. p. 145—145·5°, $[\alpha]_D^{23}$ +68·4° (*c* 0·7) (Found: C, 51·0; H, 6·1; S, 8·4%).

Reactions of Hydrazine Hydrate with Esters of Carboxylic Acids.—Unless stated, the reactions were carried out with hydrazine hydrate in ethanol solution, as described above.

Methyl 4 : 6-*O*-benzylidene-α-D-glucoside was obtained from the 2 : 3-diacetate (in 78% yield), from the 2 : 3-dibenzenesulphinate (53%), and from the 2 : 3-dibenzoate (71%, after 14 hours' reaction). The solution resulting from treatment of 1 : 2-3 : 5-di-*O*-methylene-D-glucose 6-acetate was evaporated to a syrup which was chromatographed in benzene–chloroform. Benzene eluted no product, but chloroform removed a colourless syrup. Long needles of acetamide (44%), m. p. 80—81°, were removed from the syrup by sublimation at 100°/13

[11] Bolliger and Prins, *Helv. Chim. Acta*, 1945, **28**, 465.

mm. The residual syrup crystallised with difficulty from ethanol–light petroleum to 1 : 2-3 : 5-di-*O*-methylene-D-glucose (59%), m. p. 62—63°, $[\alpha]_D^{22}$ +42·5° (*c* 0·8 in EtOH). Schmidt, Distelmaier, and Reinhard [22] record m. p. 63°, $[\alpha]_D^{20}$ + 43·8° (EtOH).

After reaction of 1 : 2-5 : 6-di-*O*-*cyclo*hexylidene-D-glucose 3-benzoate the solution was evaporated to a syrup which was chromatographed in benzene. Elution with this solvent yielded a solid which, recrystallised from methanol, was unchanged starting compound (52%), m. p. 110—111°. Washing the column with chloroform afforded a solid which, recrystallised from *n*-heptane, was 1 : 2-5 : 6-di-*O*-*cyclo*hexylidene-D-glucose (31%), m. p. 132—133°. Final elution with ethanol yielded benzamide (14%), m. p. 125—126°.

On repetition of the experiment with Raney nickel present throughout the heating with hydrazine hydrate, unchanged starting compound (84%), 1 : 2-5 : 6-di-*O*-*cyclo*hexylidene-D-glucose (7%), and benzamide (3%) were obtained.

14 Hours' boiling without catalyst gave unchanged starting compound (1%) and 1 : 2-5 : 6-di-*O*-*cyclo*hexylidene-D-glucose (90%). On elution of the chromatographic column with chloroform–ethanol (10 : 1) the early fractions, recrystallised from chloroform–light petroleum, yielded benzamide (7%). Final elution with ethanol gave, after recrystallisation from ethanol–light petroleum, benzhydrazide (33%), m. p. 111—112°.

Reaction of 1 : 2-5 : 6-di-*O*-*iso*propylidene-D-glucose 3-benzoate for 5·5 hr. afforded unchanged starting compound (4%), 1 : 2-5 : 6-di-*O*-*iso*propylidene-D-glucose (74%), benzamide (4%), and benzhydrazide (36%).

Catalytic Hydrogenation of Sugar Nitrates.—A solution of the nitrate (0·5 g.) in methanol (20 ml.) was shaken with palladium–charcoal (0·25 g.) in hydrogen at room temperature and atmospheric pressure, filtered, and evaporated. The results are summarised in the annexed Table.

Compound reduced	Yield (%) of alcohol	M. p.	Reaction time (hr.)
1 : 2-5 : 6-Di-*O*-*cyclo*hexylidene-D-glucose 3-nitrate	99	133—134°	1·5
Methyl 4 : 6-*O*-benzylidene-α-D-glucoside 2 : 3-dinitrate	98	163—164	2·5
1 : 3-2 : 4-Di-*O*-ethylidenesorbitol 5 : 6-dinitrate	100	210—212	3·5
Methyl α-D-glucoside 2 : 3 : 4 : 6-tetranitrate	96	165—166	4·5

Reaction of cyclo*Hexyl Nitrate with Sodium Iodide.*—A sealed tube containing sodium iodide (15 g., 0·1 mole) and *cyclo*hexyl nitrate (5·80 g., 0·04 mole) dissolved in anhydrous methanol (40 ml.) was heated at 100° for 44 hr. The mixture was then distilled and the residue was found to contain sodium nitrate (88%) and free iodine (3·3%), but no nitrite. The distillate, b. p. 48—77°, containing *cyclo*hexene (69%),[23] was made up to 100 ml. with carbon tetrachloride. A solution of bromine (1·8 g.) in carbon tetrachloride (20 ml.) was added during 20 min. to half of the solution at 0° with stirring. Solvents and excess of *cyclo*hexene were evaporated and the residue, after being distilled under reduced pressure, was 1 : 2-dibromo*cyclo*hexane (1·90 g.), b. p. 100—102°/12 mm.

Reaction for 66 hr. yielded *cyclo*hexene (75%), free iodine (2·2%), and sodium nitrate (95%).

Reaction of 1 : 3-O-*Benzylideneglycerol 2-Nitrate with Sodium Iodide.*—A sealed tube containing the 2-nitrate (4·50 g.) and sodium iodide (9·0 g.) dissolved in anhydrous methanol (40 ml.) was kept at 100° for 44 hr. The mixture was evaporated and chloroform and water were added to the residue which contained free iodine (3·3%) and sodium nitrite (2·6%). The chloroform solution was evaporated and the residue was chromatographed in benzene. Elution with this solvent yielded unchanged starting compound (3·73 g., 83%), m. p. 93—93·5° (from methanol). Further elution with chloroform afforded a solid which, recrystallised from *iso*propyl alcohol–light petroleum (1 : 1), was 1 : 3-*O*-benzylideneglycerol [24] (0·06 g., 2%), m. p. 82—83°.

When the experiment was repeated but with a reaction time of 90 hr. unchanged compound (71%) and the corresponding alcohol (5%) were obtained.

Reaction of trans-cyclo*Hexane*-1 : 2-*diol Dinitrate with Sodium Iodide.*—A solution of the dinitrate (4·12 g.) and sodium iodide (18 g.) in *n*-propyl alcohol (150 ml.) was boiled under reflux for 5 days. The residue obtained on evaporation was extracted with chloroform, and the combined extracts were washed with aqueous sodium thiosulphate. The chloroform solution was evaporated and the residue was chromatographed in benzene. Elution with

[22] Schmidt, Distelmaier, and Reinhard, *Chem. Ber.*, 1953, **86**, 741.
[23] Wild, " Estimation of Organic Compounds," Univ. Press, Cambridge, 1953, p. 14.
[24] Verkade and van Roon, *Rec. Trav. chim.*, 1942, **61**, 831.

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benzene–light petroleum (1 : 4) yielded unchanged starting compound (2·40 g., 58%). On washing the column with chloroform, a dark liquid was obtained which, on distillation under reduced pressure, yielded an unidentified colourless liquid (0·05 g.), b. p. 126—130°/14 mm. Ethanol removed *trans*-diol (0·08 g., 4%).

Reaction of 1 : 3-2 : 4-*Di*-O-*ethylidenesorbitol* 5 : 6-*Dinitrate with Sodium Iodide.*—A sealed tube containing the dinitrate (3·24 g., 0·01 mol.) and sodium iodide (4·5 g., 0·03 mol.) dissolved in acetone (50 ml.) was kept at 100° for 2 hr. The mixture was treated as in the previous experiment. Elution of the column with benzene–light petroleum (1 : 1) yielded, in the early fractions, a syrup which, crystallised from light petroleum, was unchanged starting compound (1·14 g., 35%), m. p. 80—80·5°. Next, benzene–light petroleum followed by benzene removed a solid which recrystallised from ethyl acetate in needles of 5 : 6-didehydro-5 : 6-dideoxy-1 : 3-2 : 4-di-*O*-ethylidenesorbitol (0·28 g., 14%), m. p. 122—123°, $[\alpha]_D^{20}$ −24·3° (*c* 1·8). Bladon and Owen [10] record m. p. 122—123°, $[\alpha]_D^{21}$ −23·8°. Washing the column with chloroform gave a syrup which crystallised from ethanol–light petroleum in prisms of 1 : 3-2 : 4-*di*-O-*ethylidenesorbitol* 6-*nitrate* (0·34 g., 12%), m. p. 129·5—130°, $[\alpha]_D^{23}$ +12·9° (*c* 7·0) (Found: C, 43·3; H, 5·9; N, 4·6. $C_{10}H_{17}O_8N$ requires C, 43·0; H, 6·1; N, 5·0%).

After reaction for 21 hr. the products were 5 : 6-didehydro-5 : 6-dideoxy-1 : 3-2 : 4-di-*O*-ethylidenesorbitol (51%) and the 6-nitrate (8%).

Characterisation of 1 : 3-2 : 4-*Di*-O-*ethylidenesorbitol* 6-*Nitrate.*—Toluene-*p*-sulphonyl chloride (0·83 g.) in pyridine (2 ml.) was added to a solution of the 6-nitrate (1·12 g.) in pyridine (2 ml.) at 0°. After 3 days at room temperature the mixture was poured into ice-water. The resulting solid, recrystallised from methanol, yielded prisms of 1 : 3-2 : 4-*di*-O-*ethylidenesorbitol* 6-*nitrate* 5-*toluene*-p-*sulphonate* (1·28 g., 74%), m. p. 111—112°, $[\alpha]_D^{21}$ +6·3° (*c* 3·9) (Found: C, 47·5; H, 5·2; S, 7·1. $C_{17}H_{23}O_{10}NS$ requires C, 47·1; H, 5·3; S, 7·4%).

A solution of this ester (0·87 g.) and hydrazine hydrate (0·30 g.) in ethanol (9 ml.) was boiled under reflux with a little Raney nickel for 1·5 hr. Excess of hydrazine was decomposed by boiling the solution with more nickel and the solution, after being filtered, was evaporated. The resulting solid (0·75 g., 96%), m. p. 127—128°, recrystallised from methanol in needles of 1 : 3-2 : 4-*di*-O-*ethylidenesorbitol* 5-*toluene*-p-*sulphonate*, m. p. 128°, $[\alpha]_D^{25}$ −29·1° (*c* 2·8) (Found: C, 52·7; H, 5·9; S, 7·9. $C_{17}H_{24}O_8S$ requires C, 52·6; H, 6·2; S, 8·3%).

A solution of this ester (0·26 g.) and benzoyl chloride (0·12 g.) in pyridine (1·5 ml.) was left at room temperature for 22 hr., then poured into ice-water and the precipitate was chromatographed. Elution with ether yielded a solid which, recrystallised from light petroleum, gave soft needles of 1 : 3-2 : 4-di-*O*-ethylidenesorbitol 6-benzoate 5-toluene-*p*-sulphonate (0·18 g., 55%), m. p. 122—123°, $[\alpha]_D^{24}$ +9·3° (*c* 2·4) (Found: C, 58·5; H, 6·0. Calc. for $C_{24}H_{28}O_9S$: C, 58·5; H, 5·7%). Matheson and Angyal [25] record m. p. 121°, $[\alpha]_D^{23}$ +5·5°.

*Reactions of Nitrates with Sodium Nitrite in Aqueous Ethanol.—trans-cyclo*Hexane-1 : 2-diol dinitrate (6·18 g., 0·03 mol.) and sodium nitrite (12·4 g., 0·18 mol.) were boiled under reflux in 70% ethanol (60 ml.) for 6 days. Water (30 ml.) was then added and the solution was continuously extracted with chloroform. Evaporation of the chloroform solution yielded a dark liquid which was chromatographed in benzene. Elution with light petroleum yielded unchanged compound (4·58 g., 74%). Chloroform removed a crude unidentified liquid (0·06 g.), and ethanol eluted the *trans*-diol (0·09 g., 3%), characterised as its dibenzoate.

A solution of 1 : 3-2 : 4-di-*O*-ethylidenesorbitol 5 : 6-dinitrate (5·84 g.) and sodium nitrite (3·7 g.) in 80% ethanol (50 ml.) was boiled under reflux for 101 hr. The brown solution was evaporated and the residue was extracted twice with chloroform. Evaporation of the combined chloroform solutions yielded a syrup which was chromatographed in benzene. Elution with this solvent yielded a syrup which, crystallised from ethanol–light petroleum, was unchanged starting compound (0·71 g., 12%). Elution with chloroform yielded a partly crystalline substance which, recrystallised from ethanol–light petroleum, was 1 : 3-2 : 4-di-*O*-ethylidenesorbitol 6-nitrate (1·25 g., 25%). Final elution with ethanol yielded a solid which, recrystallised from ethanol, was 1 : 3-2 : 4-di-*O*-ethylidenesorbitol (0·48 g., 11%).

After reaction for 23 hr., there was negligible discoloration and the products were unchanged starting compound (50%) and the 6-nitrate (15%).

Reaction of trans-cyclo*Hexane*-1 : 2-*diol Dinitrate with Concentrated Sulphuric Acid.*—The dinitrate (4·1 g., 0·02 mol.) was added with shaking during 10 min. to cold concentrated sulphuric acid (12 ml.). The resulting solution was poured into water and the clear aqueous solution was

[25] Matheson and Angyal, *J.*, 1952, 1133.

neutralised with barium carbonate. The filtrate was evaporated and the resulting solid residue (7·2 g.) was extracted with boiling 80% ethanol (400 ml.). The insoluble portion and the first crop of crystals which separated from the aqueous ethanol were barium nitrate (1·6 g.). The second crop of clustered needles, *barium* trans-cyclo*hexane*-1 : 2-*diol di*(*hydrogen sulphate*) (3·75 g., 46%), was recrystallised twice from 80% ethanol (Found: Ba, 33·39, 33·41. $C_6H_{10}O_8S_2Ba$ requires Ba, 33·37%).

When the reaction solution was left at room temperature for 1 hr., 13 hr., or 30 hr. the same yield of the same product was obtained.

Just enough N-sulphuric acid was added to saturated aqueous barium *trans-cyclo*hexane-1 : 2-diol di(hydrogen sulphate) (8·22 g.) to precipitate all the barium as sulphate. This was removed by centrifugation, and phenylhydrazine (4·10 g.) dissolved in ethanol (10 drops) was added to the solution. Concentration of the solution yielded white crystals of trans-cyclo*hexane*-1 : 2-*diol di*(*hydrogen sulphate*) *bisphenylhydrazine salt* (7·18 g., 73%), m. p. 181—181·5° (decomp.), which after one recrystallisation from *n*-propyl alcohol had m. p. 182·5—183° (decomp.) [Found: equiv., 246·6; C, 43·8; H, 5·8; S, 12·6%. $C_6H_{12}O_8S_2.(C_6H_5{\cdot}NH{\cdot}NH_2)_2$ requires equiv., 246·3; C, 43·9; H, 5·7; S, 13·0%]. The salt decomposed after two or more recrystallisations from boiling *n*-propyl alcohol and had m. p. ~177° (decomp.), varying considerably with the rate of heating. After prolonged storage at room temperature in a securely stoppered tube the salt also decomposed.

Reaction of trans-cyclo*Hexane*-1 : 2-*diol with Concentrated Sulphuric Acid.*—Powdered *trans-cyclo*hexane-1 : 2-diol (5·8 g., 0·05 mol.) was stirred into cold concentrated sulphuric acid (20 ml.) during 10 min. The resulting solution was immediately poured into water, and the clear aqueous solution was neutralised with barium carbonate. Evaporation of the filtered solution yielded a white solid (16·7 g., 75%) which recrystallised from 75% ethanol in fine needles of the *dihydrate* of barium *trans-cyclo*hexane-1 : 2-diol di(hydrogen sulphate) (Found: Ba, 30·5, 30·7; loss in wt. at 75°/0·02 mm., 8·50. $C_6H_{10}O_8S_2Ba,2H_2O$ requires Ba, 30·7; H_2O, 8·0%. Found for the anhyd. *salt*: Ba, 33·3, 33·4%).

The bisphenylhydrazine salt had m. p. 182·5—183° (decomp.), undepressed on admixture with a sample prepared from the dinitrate (Found: equiv., 245·1).

A saturated aqueous solution of the di(hydrogen sulphate) was kept at 93° for 17 hr. Continuous extraction of the resulting solution with chloroform yielded *trans-cyclo*hexane-1 : 2-diol (52%) which, recrystallised from acetone, had m. p. 103·5—104°.

Reaction of cis-cyclo*Hexane*-1 : 2-*diol Dinitrate with Concentrated Sulphuric Acid.*—The *cis*-dinitrate (5·15 g.) was treated in a similar manner to the *trans*-isomer except that the mixture of barium salts was extracted with cold dimethylformamide (30 ml.), leaving undissolved barium nitrate (2·3 g.). The solvent was evaporated and the residue was crystallised from 70% ethanol (300 ml.), giving large needles of *barium* cis-cyclo*hexane*-1 : 2-*diol di*(*hydrogen sulphate*) *dihydrate* (4·5 g., 40%) which was recrystallised twice from 70% ethanol (Found: Ba, 30·4, 30·5%). The *anhydrous salt* was obtained on heating the dihydrate at 85°/0·03 mm. (Found: Ba, 33·2, 33·2%).

The procedure used for the *trans*-isomer was employed to make cis-cyclo*hexane*-1 : 2-*diol di*(*hydrogen sulphate*) *bisphenylhydrazine salt* (74%), m. p. 160—161° (decomp.) (Found: equiv., 246·6; C, 44·0; H, 5·6%). This compound decomposed on being kept in a securely stoppered tube at room temperature for several weeks.

Reaction of cis-cyclo*Hexane*-1 : 2-*diol with Concentrated Sulphuric Acid.*—The procedure used for the *trans*-isomer gave barium *cis-cyclo*hexane-1 : 2-diol di(hydrogen sulphate) dihydrate (70%) which was recrystallised from 62% ethanol (Found: Ba, 30·45, 30·4%).

The bisphenylhydrazine salt had m. p. 160—161° (decomp.), undepressed on admixture with a sample prepared from *cis-cyclo*hexane-1 : 2-diol dinitrate (Found: equiv., 246·6).

The *cis*-diol (72%) was obtained after a saturated aqueous solution of the di(hydrogen sulphate) had been heated at 92° for 24 hr.

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525. *Heats of Combustion and Molecular Structure. Part VI.* The Structure of Some Cyclic Ethers of o-Dihydroxybenzene.*

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The heats of combustion of *o*-dimethoxybenzene, 1 : 3-dioxaindane, 1 : 4-dioxatetralin, and 2 : 3-benzo-1 : 4-dioxa*cyclo*heptane have been measured. The resonance energies are derived and are discussed in terms of the structures of the non-aromatic groupings.

Experimental

Materials.—*o*-Dimethoxybenzene (from Messrs. Hopkin and Williams) was distilled through a 6" Fenske column. The fraction collected had b. p. 205·5°/748 mm. Heilbron and Bunbury [1] give b. p. 206°/759 mm.

1 : 3-Dioxaindane (1 : 3-benzodioxole) was prepared by the method suggested by Baker,[2] from methylene sulphate and *o*-dihydroxybenzene. Distilled through an 18" Fenske column, the fraction collected had b. p. 173·2—173·5°/758 mm. Baker [2] gives b. p. 173—174°/756 mm.

1 : 4-Dioxatetralin (2 : 3-dihydrobenzo-1 : 4-dioxan) was prepared from ethylene bromide and *o*-dihydroxybenzene in the presence of potassium carbonate, copper bronze, and glycerol.[3] It distilled at 213·2°/774 mm. Gattermann [3] gives b. p. 206—207°/749 mm.

2 : 3-Benzo-1 : 4-dioxa*cyclo*heptene (6 : 7-dihydro-2 : 3-benzo-1 : 4-dioxepin) was prepared by heating *o*-dihydroxybenzene (27·5 g.), 1 : 3-dibromopropane (50 g.), finely powdered anhydrous potassium carbonate (35 g.), glycerol (1 g.), and copper bronze (1 g.) under reflux for 10 hr.[4] The mixture was cooled, diluted with water (30 ml.), and made faintly alkaline with sodium hydroxide, then steam-distilled, and the distillate was extracted with chloroform. The chloroform layer was separated, dried (Na_2SO_4), and distilled. The product was distilled through a 6" Fenske column, the fraction collected having b. p. 100·5°/11 mm (Found: C, 72·0; H, 6·6. Calc. for $C_9H_{10}O_2$: C, 72·0; H, 6·7%).

Vapour-pressure Measurement.—The vapour pressures of the compounds were measured in an apparatus of the type described by Sanderson.[5] The values of A and B of the equation $\log_{10} p_{mm.} = -A/T + B$ are given in Table 1. The derived latent heats of vaporisation (liquid to vapour), given by $L_v = 4{\cdot}57A \times 10^{-3}$ kcal./mole, are also listed.

Table 1.

Compound	A	B	L_v (kcal./mole)
o-Dimethoxybenzene	3492·0	9·58	16·0
1 : 3-Dioxaindane	2164·1	7·69	9·90
1 : 4-Dioxatetralin	2633·7	8·27	12·05
2 : 3-Benzo-1 : 4-dioxa*cyclo*heptene	2918·3	8·8	13·28

Combustion Calorimetry.—*o*-Dimethoxybenzene was burnt in a twin-valve bomb (The Parr Instrument Company, Moline, Illinois, U.S.A.) of energy equivalent, $E = 39{,}058 \pm 20$ cal./ohm, the temperature changes being recorded by a platinum resistance thermometer. Details of the experimental procedure and method of calculation have been given in Parts III and IV of this series. The amount of carbon dioxide present in the bomb gases after combustion was determined; the theoretical quantity was deficient by an amount which corresponded closely to the weight of carbon remaining in the bomb after combustion. A correction was made by taking the heat of combustion of amorphous carbon as 8·11 kcal./g. Combustions of the remaining compounds were made in a stainless-steel, single-valve, Mahler–Cook bomb of energy equivalent, $E = 31{,}199 \pm 8{\cdot}0$ cal./ohm, according to the procedure described in Part III. The results are shown in Table 2.

* Parts I—V, *Trans. Faraday Soc.*, 1954, **50**, 815; *J.*, 1954, 2764; 1955, 1188; 1958, 958, 1406.

[1] Heilbron and Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.

[2] Baker, *J.*, 1931, 1765.

[3] Gattermann, *Annalen*, 1907, **375**, 373.

[4] Ghosh, *J.*, 1915, **107**, 1591.

[5] Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, New York, 1948, p. 48.

TABLE 2.

Weight taken * (*m*) (g.)	ΔR (ohms)	Corrections (cal.) Fuse	HNO_3	Carbon	*C* (cal./ohm)	$-\Delta U_b$ (kcal./mole)
		o-*Dimethoxybenzene*, *M* 138·16				
0·6606	0·12555	14·3	2·4	8·9	4·8	1023·9
0·3951	0·07509	17·9	1·3	13·9	2·4	1023·5
0·5701	0·10851	16·3	2·0	7·7	4·1	1024·5
0·3648	0·06902	14·8	1·3	3·9	2·6	1025·2
		1 : 3-*Dioxaindane*, *M* 122·12				
0·9977	0·21553	113·7	0·1	0·3	7·0	820·5
0·9726	0·20910	89·9	0·2	0·8	7·0	819·5
1·0014	0·21491	80·1	0·7	0·8	7·0	819·1
		1 : 4-*Dioxatetralin*, *M* 136·14				
1·0356	0·23776	84·7	3·4	0·7	8·0	964·8
0·69305	0·15933	59·5	0·2	3·9	4·0	965·1
0·66713	0·15346	67·4	0·2	3·5	4·0	964·4
		2 : 3-*Benzo*-1 : 4-*dioxa*cyclo*heptene*, *M* 150·17				
0·9454	0·23102	87·8	1·4	—	6·0	1130·4
0·8915	0·21032	83·4	2·1	2·9	6·0	1130·2
0·8244	0·20193	93·0	2·5	0·3	6·0	1130·1

Where $-\Delta U_b = (M/m)[(E + C)\Delta R - \text{corr.}_{\text{fuse}} - \text{corr.}_{HNO_3} + \text{corr.}_{\text{carbon}}] \times 10^{-3}$ kcal./mole.

* Weight *in vacuo*.

The $-\Delta U_b$ terms were converted into $-\Delta H_c^\circ$ terms, the standard heat of combustion (Table 3), by using the expression

$$-\Delta H_c^\circ = -\Delta U_b - w - \Delta n\boldsymbol{R}T,$$

where w is the Washburn correction, calculated by Prosen's method,[6] and Δn is the number of moles of gas produced in the combustion.

TABLE 3.

Compound	$-\Delta U_b$ mean (kcal./mole)	Standard deviation ($-\Delta U_b$) (%)	Overall standard deviation (%)	Washburn corr. w (kcal./mole)	$\Delta n\boldsymbol{R}T$ (kcal./mole)	$-\Delta H_c^\circ$ (kcal./mole)
o-Dimethoxybenzene	1024·2	0·047	0·050	0·6	−0·3	1023·9 ± 0·5
1 : 3-Dioxaindane ...	819·6	0·061	0·072	0·6	−0·3	819·3 ± 0·5
1 : 4-Dioxatetralin ...	964·8	0·028	0·035	0·7	−0·6	964·7 ± 0·3
2 : 3-Benzo-1 : 4-dioxa-*cyclo*heptene	1130·2	0·018	0·020	0·8	−0·9	1130·3 ± 0·2

DISCUSSION

The $-\Delta H_{f,g}^{st}$ terms for the compounds were calculated from $-\Delta H_c^\circ$ and L_v terms by using $\Delta H_f^\circ H_2O(l.) = -68{\cdot}32$ and $\Delta H_f^\circ CO_2(g.) = -94{\cdot}05$ kcal./mole. By incorporating the ΔH_a terms, C, 171·7;[7] H, 52·09;[8] O, 58·98 kcal./g.-atom,[9] the $-\Delta H_{f,g}^a$ terms were derived. A summation was made of the mean bond-energy terms in the molecule, $\Sigma\bar{E}(b)$, the values $\bar{E}$(C–C), 83·1; $\bar{E}$(CH=CH, *cis*), 148·2; $\bar{E}$(C–H), 98·85 (Part II); and $\bar{E}$(C–O), 84·3 kcal./mole, being used (Part V). The difference, $-\Delta H_{f,g}^a - \Sigma\bar{E}(b) = E_r$, was evaluated. These values are given in Table 4.

The variation in the resonance energy is correlated with the difference in structure of the non-aromatic rings.

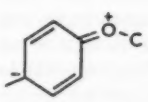
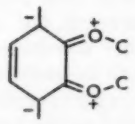
It has been shown in Part V that the resonance energy of the C_6H_5O system is of the order of 42 kcal./mole, due to contributions from ionic forms of the type (I). (The resonance energy of the C_6H_5C system is 38·9 kcal./mole.)

[6] Prosen, " Experimental Thermochemistry," ed. Rossini, Interscience, New York, 1956.
[7] Brewer and Kane, *J. Phys. Chem.*, 1955, **59**, 105.
[8] Nat. Bur. Stand., Circular 500, Washington, 1952.
[9] Brix and Herzberg, *J. Chem. Phys.*, 1953, **21**, 2240.

TABLE 4.

Compound	$-\Delta H_{f,g}$[a]	$\Sigma\overline{E}(b)$ (kcal./mole)	E_r (kcal./mole)
o-Dimethoxybenzene	2066·6	2019·6	47·0
1 : 3-Dioxaindane	1664·2	1625·8	38·4
1 : 4-Dioxatetralin	1954·4	1906·6	47·8
2 : 3-Benzo-1 : 4-dioxa*cyclo*heptene	2225·5	2187·4	38·1

It is to be expected that the resonance energy of the *o*-$C_6H_4O_2$ system will exceed that of the C_6H_5O system, owing to the increased number of ionic forms [including those of the type (II)].

(I)   (II)

The resonance energies for *o*-dimethoxybenzene and 1 : 4-dioxatetralin are some 5 kcal./mole greater than for the C_6H_5O system, while those for 1 : 3-dioxaindane and 2 : 3-benzo-1 : 4-dioxa*cyclo*heptene are about 4 kcal./mole less. Resonance of types (I) and (II) is favoured if (i) the $C_{ar.}$–O–$C_{al.}$ angle can be 121° ± 2°,[10] and (ii) if the O–$C_{al.}$ fragment of the side-chain can be coplanar with the aromatic nucleus. A simple consideration of scale models, with 110° for the unstrained $-CH_2-$ angle, and the normal interatomic distances $C_{ar.}$–O, 1·36 Å;[10] $C_{al.}$–O, 1·42 Å; and $C_{al.}$–$C_{al.}$, 1·54 Å [11] shows that the conditions (i) and (ii) can be satisfied with *o*-dimethoxybenzene and with 1 : 4-dioxatetralin, but not with 1 : 3-dioxaindane, in which, though the whole molecule is planar, the $C_{ar.}$–O–$C_{al.}$ angle must be much less than 125°, or with 2 : 3-benzo-1 : 4-dioxa*cyclo*heptene. These steric considerations are thus compatible with the experimental findings and with those from dipole-moment studies.[12]

UNIVERSITY COLLEGE OF NORTH STAFFORDSHIRE,
KEELE, STAFFS.

[*Received, February 17th*, 1958.]

[10] Goodwin, Przyblska, and Robertson, *Acta Cryst.*, 1950, **3**, 279.
[11] Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.
[12] Springall, Hampson, May, and Spedding, *J.*, 1949, 1524.

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526. *Heteropolytungstic Acids and Heteropolytungstates. Part III.** 12-*Tungstozincic Acid and its Salts, and Some* 12-*Tungsto*-3-*zincates.*

By DONALD H. BROWN and JOHN A. MAIR.

Zinc forms two heteropoly-acids with tungsten, a 3 : 12- and a 1 : 12-acid. The 3 : 12-acid was only identified through its salts, as the free acid was not isolated. The 1 : 12-acid was isolated, as were a number of its salts. The structure of cæsium 12-tungstozincate was shown to be similar to that of cæsium 12-tungstophosphate.

THE methods of preparation of the heteropoly-acids of zinc and tungsten involve the addition of a zinc salt to a hot solution of sodium paratungstate or metatungstate. The salts of 12-tungsto-3-zincic acid, which have solubilities comparable with those of the corresponding normal paratungstates, are removed by fractional crystallisation. The 12-tungstozincic acid is extracted from the mother-liquors by the formation of the ether addition compound.[1]

The salts obtained of 12-tungsto-3-zincic acid showed different apparent basicities,

* Part II, *J.*, 1950, 2372.

[1] Drechsel, *Ber.*, 1887, **20**, 1452.

a maximum of nine being exhibited in the guanidine and nickel salts. When the salts were heated in a thermal balance no apparent break was observed in the curve of water lost versus temperature. Thus, presumably, the oxide lattice broke down before the salt was completely dehydrated. In an attempt to obtain the free acid, a solution of the sodium salt was passed through a cation-exchange resin saturated with hydrogen ions. The effluent was shown to contain a mixture of 12-tungstozincic acid and metatungstic acid. Both zinc and tungsten were retained in the column. The passage of the sodium salt solution down the column can be compared to a slow acidification. This was confirmed by slowly acidifying a solution of the sodium salt during 6 hours at about 90°. Again some 12-tungstozincic acid and some metatungstic acid were obtained.

From the original preparations the 12-tungstozincic acid was isolated as a yellow crystalline solid. Its solubility was comparable to that of metatungstic acid from which it was separated by baking on a steam-bath. Because of the low thermal stability of metatungstic acid it decomposed, giving tungstic acid and leaving as the only soluble product 12-tungstozincic acid. To determine the basicity of the acid, a sample was heated on the thermal balance. No break in the curve was observed, again probably because the oxide lattice broke down during dehydration. A solution of 12-tungstozincic acid, titrated potentiometrically against sodium hydroxide solution, gave a mean equivalent weight of 572. From the molecular weight of $ZnO,12WO_3,29H_2O$, for a six-basic acid, the equivalent weight is 565. These results are sufficiently close to suggest that the acid has a basicity not greater than six. This is confirmed in the majority of the salts prepared. 12-Tungstozincic acid was found, by displacement of toluene from a density bottle, to have a density of 4·14 g./c.c.

12-Tungstozincic acid and its salts resemble closely in chemical behaviour 12-tungstophosphoric acid and its salts. Keggin [2] and Santos [3] analysed the structures of 12-tungstophosphoric acid and cæsium 12-tungstophosphate. The cæsium salt of 12-tungstozincic acid was used for comparison as there always appeared to be slight decomposition, with subsequent formation of tungstic acid, from 12-tungstozincic acid itself. Powder photographs were taken with the specimen mounted in a fine Lindemann-glass tube. The structure was found to be cubic with a unit-cell length 11·86 Å. This value is close to that (11·83 Å) found by Santos for cæsium 12-tungstophosphate. The intensities were measured and found to agree with those calculated from a structure similar to that proposed for cæsium 12-tungstophosphate, but with zinc as the central atom.

Experimental

Two methods of preparation were used.

(1) Sodium tungstate dihydrate (56·2 g.), dissolved in water (400 ml.), was converted into the paratungstate by addition of N-nitric acid (198·6 ml.) and boiling the mixture. To the solution was added with stirring a solution of zinc nitrate (10 g.) in water (700 ml.) during 20 hr. The temperature of the paratungstate solution was kept about 80—90°. Higher temperatures caused partial hydrolysis of the products to zinc paratungstate.

(2) Sodium tungstate dihydrate (56·2 g.) in water (400 ml.) was converted into the metatungstate by boiling it with N-nitric acid (255·4 ml.). Zinc oxide (10 g.) was added during 5 days to the stirred metatungstate solution at about 80—90°.

The solutions obtained by either method were filtered hot, then concentrated slowly to about 150 ml. and set aside. Small white crystals separated, which recrystallised from water. The different methods of preparation gave salts with differing analyses but each yielded an ammonium salt of the same composition. The salts obtained appeared to be different sodium zinc salts of 12-tungsto-3-zincic acid.

The mother-liquors were extracted with ether and 12N-sulphuric acid. The ether addition compound formed was purified by dropping it through several portions of ether. On dilution

[2] Keggin, *Proc. Roy. Soc.*, 1934, *A*, **144**, 75.
[3] Santos, *ibid.*, 1935, *A*, **150**, 309.

with water, the ether separated and was removed by evaporation. The aqueous solution was evaporated to dryness on a steam-bath and the tungstic acid, formed by the decomposition of the metatungstic acid present, removed by filtration. The process was repeated until little tungstic acid was precipitated. The final aqueous extract was concentrated to small bulk, first on the steam-bath and then over concentrated sulphuric acid in a partial vacuum. Yellow crystals of **12-*tungstozincic acid*** separated (Found: ZnO, 2·42; WO_3, 82·4; H_2O, 15·3. $ZnO,12WO_3,29H_2O$ requires ZnO, 2·42; WO_3, 82·2; H_2O, 15·4%).

Salts of **12-*Tungsto*-3-*zincic Acid*.**—***Ammonium salt*.** This *salt* was prepared by adding a hot saturated solution of ammonium chloride to a hot solution of sodium 12-tungsto-3-zincate. The solution was filtered hot and set aside. On cooling, colourless crystals separated which recrystallised from water [Found: NH_4, 4·1; ZnO, 7·3; WO_3, 80·7; H_2O, 6·0. $4(NH_4)_2O,3ZnO,12WO_3,11H_2O$ requires NH_4, 4·1; ZnO, 7·1; WO_3, 81·1; H_2O, 5·8%].

Nickel salt. The *nickel salt* was prepared by adding a hot saturated solution of nickel nitrate to a hot solution of the ammonium salt, filtering and cooling. Green crystals separated, which recrystallised from water (Found: NiO, 8·22; ZnO, 6·2; WO_3, 68·9; H_2O, 17·5. $4·5NiO,3ZnO,12WO_3,39H_2O$ requires NiO, 8·3; ZnO, 6·1; WO_3, 68·4; H_2O, 17·3%).

Guanidine salt. This *salt* was prepared by adding 5% aqueous guanidine hydrochloride to a dilute solution of the ammonium salt. If the temperature was kept at about 80°, the precipitate was formed slowly. The resulting small colourless crystals were only slightly soluble in water [Found: CH_6N_3, 14·7; ZnO, 6·3; WO_3, 72·4; H_2O, 5·9; $4·5(CH_6N_3)_2O,3ZnO,12WO_3,12·5H_2O$ requires CH_6N_3, 14·8; ZnO, 6·3; WO_3, 72·0; H_2O, 5·8%].

Salts of **12-*Tungstozincic Acid*.**—***Ammonium salt*.** The *ammonium salt* was prepared by adding a hot concentrated solution of ammonium chloride to a hot concentrated solution of 12-tungstozincic acid, then filtering and cooling the mixture. The salt, which separated as colourless crystals, recrystallised rom water [Found: NH_4, 3·1; ZnO, 2·5; WO_3, 84·8; H_2O, 8·3. $3(NH_4)_2O,ZnO,12WO_3,15H_2O$ requires NH_4, 3·3; ZnO, 2·5; WO_3, 84·6; H_2O, 8·2%].

Barium salt. This *salt* was prepared by neutralising a solution of 12-tungstozincic acid with barium carbonate, then filtering and cooling the mixture. The salt separated as colourless crystals, which recrystallised from water (Found: BaO, 12·1; ZnO, 2·18; WO_3, 72·9; H_2O, 13·1. $3BaO,ZnO,12WO_3,28H_2O$ requires BaO, 12·0; ZnO, 2·12; WO_3, 72·7; H_2O, 13·2%).

Guanidine salt. This *salt* was prepared by adding 5% aqueous guanidine hydrochloride to a solution of 12-tungstozincic acid. Filtration and cooling gave white crystals which recrystallised from water [Found: CH_6N_3, 11·2; ZnO, 2·4; WO_3, 82·3; H_2O, 3·35. $3(CH_6N_3)_2O,ZnO,12WO_3,6H_2O$ requires CH_6N_3, 11·3; ZnO, 2·4; WO_3, 82·3; H_2O, 3·2%].

Analyses.—Barium was determined as the sulphate by precipitation with dilute sulphuric acid, the anion being stable enough to permit this. Zinc was determined by precipitation as the oxine derivative; nickel by precipitation with dimethylglyoxime; tungsten by precipitation with cinchonine hydrochloride and ignition to the oxide; ammonia by distillation into standard acid solution; water by ignition and difference; and guanidine by the micro-Dumas method.

The authors thank Mr. J. Cameron for the nitrogen microestimations. One of them (D. H. B.) is also indebted to the D.S.I.R. for a maintenance grant.

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527. *Homolytic Aromatic Substitution. Part XV.* Ratio of Isomerides formed in the Arylation of Chlorobenzene and Bromobenzene with* p-*Nitrophenyl Radicals.*

By Chang Shih, D. H. Hey, and Gareth H. Williams.

Measurements are reported of the proportions in which homolytic substitution by *p*-nitrophenyl radicals takes place at the *ortho*-, *meta*-, and *para*-positions of chlorobenzene and bromobenzene. In order to resolve inconsistencies revealed on examination of previous work, the proportions in which the 2-, 3-, and 4-isomer are formed in the phenylation of chlorobenzene have been measured. The results thus obtained illustrate the electrophilic character of the *p*-nitrophenyl radical, since significantly less *meta*-substitution takes place in *p*-nitrophenylation than in phenylation of these halogenobenzenes.

It is apparent from previous work (De Tar and Kazimi,[1] Dannley and Sternfeld,[2] Cadogan, Hey, and Williams [3]) that the nitro-group, being powerfully electron-attracting, confers considerable electrophilic character on an aryl radical in which it is situated in the *para*-position. The *p*-nitrophenyl radical is therefore used in the work described in this communication as a typical example of an electrophilic radical. Substitution in the halogenobenzenes by all types of reagents is of special interest, because of the peculiar combination of inductive and tautomeric effects ($-I + T$) exhibited by the halogens, which give rise in electrophilic substitution, as is well known, to deactivation of the nucleus accompanied by *ortho-para*-direction. Similarly the influence of a halogen atom on the nucleophilic replacement of groups present in the same nucleus is also anomalous, such replacement of groups oriented *meta* to the halogen being facilitated to a greater extent than that of groups in the *ortho*- and the *para*-position (see, for example, Bunnett and Zahler [4]). Arylation of the halogenobenzenes by electrophilic radicals is therefore of interest since, if the interpretation of the behaviour of polarised radicals put forward in Parts IX [3] and XIV [5] is correct, the modification of the pattern of substitution in the halogenobenzenes occasioned by the use of an electrophilic radical should be subject to similar influences. Thus, it may be predicted that while the relative rate of substitution by *p*-nitrophenyl radicals should be less than that of phenylation, the amount of the *meta*-isomer produced in *p*-nitrophenylation should be *less* than that produced in phenylation.

The relative rate of *p*-nitrophenylation of chlorobenzene has been shown by Cadogan, Hey, and Williams [3] to be less than that of phenylation, and similar measurements on bromobenzene are to be described in Part XVI,[6] in which partial rate factors are derived.

In the present communication measurements are reported of the ratios of isomerides obtained in the *p*-nitrophenylation of chlorobenzene and bromobenzene. Infrared spectroscopy was used for the analysis. The interest of these results lies in a comparison of them with the corresponding ratios for phenylation. The ratio of isomerides in the phenylation of chlorobenzene measured by Augood, Hey, and Williams [7] appears to be somewhat out of harmony with the results for the other halogenobenzenes which were obtained by Augood, Cadogan, Hey, and Williams,[8] and also with the results of Dannley, Gregg, Phelps, and Coleman.[9] In particular, the proportion of 3-chlorodiphenyl appears

* Part XIV, *J.*, 1958, 1885.

[1] De Tar and Kazimi, *J. Amer. Chem. Soc.*, 1955, **77**, 3842.
[2] Dannley and Sternfeld, *ibid.*, 1954, **76**, 4543.
[3] Cadogan, Hey, and Williams, *J.*, 1955, 1425.
[4] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 315.
[5] Chang, Hey, and Williams, *J.*, 1958, 1885.
[6] Chang, Hey, and Williams, *J.*, to be submitted.
[7] Augood, Hey, and Williams, *J.*, 1953, 44.
[8] Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412.
[9] Dannley, Gregg, Phelps, and Coleman, *J. Amer. Chem. Soc.*, 1954, **76**, 445.

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to be anomalously low. Accordingly, this measurement was repeated and it was indeed found that the proportion of 3-chlorodiphenyl is higher than that previously reported. These results are summarised in Table 1, in which the ratio of isomerides for the phenylation of bromobenzene obtained by Augood, Cadogan, Hey, and Williams [8] is included for completeness.

Table 1. *Ratios of isomerides formed in the phenylation and* p-*nitrophenylation of chlorobenzene and bromobenzene.*

Compound	Reaction	Composition (%) 2-	3-	4-
PhCl	Phenylation	50·1	31·6	18·3
PhCl	*p*-Nitrophenylation	59·6	24·2	16·2
PhBr	Phenylation	49·3	33·3	17·4
PhBr	*p*-Nitrophenylation	60·5	25·1	14·4

The most striking feature of these results is the substantially smaller amount of *meta*-substitution which takes place in both compounds with *p*-nitrophenyl than with phenyl radicals, in accord with the predictions made above. The compensating increase appears to be in substitution at the *ortho*- rather than the *para*-position; indeed, the amount of the 4-isomer appears to decrease slightly. The meaning of this effect at the *para*-position, if real, is at present obscure.

Experimental

Reagents.—Unless otherwise stated, the light petroleum used had b. p. 60—80°. Solids were recrystallised to constant m. p.

Benzoyl peroxide, nitromethane, and chlorobenzene were purified as described in Part II,[10] and bromobenzene as described in Part IV.[8] *p*-Nitrobenzoyl peroxide was prepared by Hey and Walker's method.[11] 2-, 3-, and 4-Chlorodiphenyl were kindly presented by Dr. P. Clarke (King's College, London), whom we thank. 2-Chlorodiphenyl was recrystallised from light petroleum (to m. p. 33·5°), and the 4-isomer from ethanol–water (to m. p. 77°). 3-Chlorodiphenyl, which was a colourless oil (n_D^{20} 1·6198), was used without further purification. The preparation of 4-chloro-4′-nitrodiphenyl and 4-bromo-4′-nitrodiphenyl was reported in Part XIV.[5] 3-Bromo-4′-nitrodiphenyl (m. p. 94—95°) was prepared by Case's method.[12]

2-Bromo-4′-nitrodiphenyl.—This was prepared by a modification of Scarborough and Waters's method.[13] A solution of 2-acetamidodiphenyl in glacial acetic acid was treated with a mixture of concentrated sulphuric acid and fuming nitric acid at 0°, the temperature being carefully controlled, to give 2-acetamido-4′-nitrodiphenyl, m. p. 201°. Hydrolysis for 1½ hr. with boiling 10% ethanolic hydrochloric acid gave 2-amino-4′-nitrodiphenyl, m. p. 158°, which was diazotised by Hodgson and Walker's method [14] as follows. A hot solution of 2-amino-4′-nitrodiphenyl (5 g.) in glacial acetic acid (47 ml.) was rapidly cooled to room temperature and added with stirring to a solution of sodium nitrite (1·78 g.) in concentrated sulphuric acid (12·5 ml.), the temperature being maintained below 20° throughout the addition. The resulting solution was added to the mixture obtained by treating a solution of copper sulphate (6·68 g.) and sodium bromide (3·23 g.) in water (21·5 ml.) with one of sodium metabisulphite (1·48 g.) and sodium hydroxide (0·98 g.) in water (11 ml.). The resulting mixture was immediately treated with 48% hydrobromic acid (7 ml.) and kept overnight. The solid residue obtained on filtration crystallised from methanol to give 2-bromo-4′-nitrodiphenyl as yellow needles, m. p. 82—83° (2 g.). Scarborough and Waters [13] reported m. p. 82·5°.

2-Chloro-4′-nitrodiphenyl.—This was prepared by a method analogous to that described above for the preparation of 2-bromo-4′-nitrodiphenyl, except that the diazotisation of 2-amino-4′-nitrodiphenyl and the subsequent Sandmeyer reaction were carried out in the presence of concentrated hydrochloric acid. 2-Chloro-4′-nitrodiphenyl was obtained as pale yellow needles, m. p. 77—78°. Case [15] reported m. p. 74—75°.

[10] Augood, Hey, and Williams, *J.*, 1952, 2094.
[11] Hey and Walker, *J.*, 1948, 2216.
[12] Case, *J. Amer. Chem. Soc.*, 1945, **67**, 118.
[13] Scarborough and Waters, *J.*, 1927, 89.
[14] Hodgson and Walker, *J.*, 1933, 1620.
[15] Case, *J. Amer. Chem. Soc.*, 1943, **65**, 2137.

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3-Chloro-4′-nitrodiphenyl.—(*a*) Dry chlorine was passed at room temperature into a solution of 2-acetamido-4′-nitrodiphenyl (4 g.) and anhydrous sodium acetate (4 g.) in glacial acetic acid (200 ml.) until a gain in weight of about 0·6 g. had occurred. After being kept overnight, the mixture was poured into ice-water, and the chlorinated product collected by filtration. Repeated crystallisation from acetone–ethanol gave 2-acetamido-5-chloro-4′-nitrodiphenyl (1·5 g.; m. p. 204—206°), which was then hydrolysed by boiling dilute sulphuric acid. The 2-amino-5-chloro-4′-nitrodiphenyl thus obtained (4 g.) was diazotised in 50% sulphuric acid (7 ml.) with a saturated aqueous solution of sodium nitrite (1·2 g.). The filtered solution of the diazonium salt was treated with 30% aqueous hypophosphorous acid (18 ml.) at 0°, and the ensuing reaction allowed to proceed at this temperature for 24 hr. Repeated crystallisation of the product from methanol gave *3-chloro-4′-nitrodiphenyl* (1 g.) as yellow needles, m. p. 89° (Found: Cl, 15·8. $C_{12}H_8O_2NCl$ requires Cl, 15·2%).

(*b*) A mixture of *m*-chloroaniline (50 g.), concentrated hydrochloric acid (79·5 ml.), and crushed ice was treated with sodium nitrite (29·7 g.) in water (55·5 ml.) until the presence of a slight excess was indicated by starch–iodide paper. After filtration, the solution was vigorously agitated with nitrobenzene (500 ml.) at 0—5°, while 5N-sodium hydroxide solution (99 ml.) was added dropwise. Stirring was continued for 3 hr. at 5°, and for a further 48 hr. at room temperature. The nitrobenzene layer was washed with water, and the solvent removed by distillation under reduced pressure. The resulting tar was extracted repeatedly with boiling light petroleum. The extracts were fractionally distilled and the orange oil (6·0 g.), b. p. 162—172°/0·7 mm., collected and redistilled, the fraction of b. p. 168—172°/0·7 mm. then being collected. Decolorisation with activated charcoal, followed by repeated crystallisation from methanol, gave 3-chloro-4′-nitrodiphenyl (3·8 g.) as pale yellow needles, m. p. 91° (Found: C, 61·7; H, 3·5; N, 5·9; Cl, 14·9. $C_{12}H_8O_2NCl$ requires C, 61·7; H, 3·4; N, 6·0; Cl, 15·2%). A mixed m. p. with the specimen prepared from 2-acetamido-4′-nitrodiphenyl showed no depression. The infrared spectra of the two specimens in nitromethane solution were identical.

Reaction of Benzoyl Peroxide with Chlorobenzene.—In experiments 1 and 2, benzoyl peroxide (6 g.) was allowed to decompose in chlorobenzene (200 ml.) in a thermostat at 80° for 72 hr. The standard procedure (Part II [10]) was used for the isolation of the diaryl fractions. In order to remove the last traces of the high-boiling resin which is formed in this reaction, the mixtures were redistilled twice. The chlorodiphenyl mixtures (b. p. 65—95°/0·15 mm.) were obtained as colourless oils, and the resins as yellow glassy solids, similar to those reported by Augood, Hey, and Williams.[7] The resins were not investigated further. The weights of the various products obtained are given in Table 2.

TABLE 2. *Products obtained in the reactions of benzoyl peroxide with chlorobenzene.*

Expt.	Diaryl fraction (g.)	Resin (g.)	Benzoic acid (g.)	Compositions of chlorodiphenyls (%) 2-	3-	4-
1	2·6810	2·4768	1·79	49·2	32·3	18·6
2	2·6202	2·3788	1·80	50·9	31·0	18·1
Mean	—	—	—	50·1	31·6	18·3

Reaction of p-*Nitrobenzoyl Peroxide with Chlorobenzene and Bromobenzene.*—In experiments 3 and 4, *p*-nitrobenzoyl peroxide (6 g.) was allowed to decompose in chlorobenzene (200 ml.) in a thermostat at 80° for 72 hr. In experiments 5 and 6, bromobenzene (200 ml.) was used as solvent. The standard procedure (Part II [10]) was used for the isolation of the diaryl fractions. The mixtures of chloro-4′-nitrodiphenyls obtained from experiments 3 and 4 (4·0120 g. and 3·9602 g. respectively) had b. p. 110—130°/0·1 mm., and the mixtures of bromo-4′-nitrodiphenyls obtained from experiments 5 and 6 (4·0275 g. and 3·9484 g. respectively) had b. p. 110—135°/0·1 mm. All these mixtures were shown by analysis to contain no extraneous material. Only very small quantities (*ca.* 0·1 g.) of high-boiling resinous material were formed in experiments 3—6.

Infrared Analysis of Mixtures of Isomers.—The mixtures of isomers obtained from experiments 1—6 were analysed by the infrared method, the procedure described in Part XIV [8] being used. The " key " absorption bands used for the analyses were as follows: 2-chloro-4′-nitrodiphenyl, 771 cm.$^{-1}$; 3-chloro-4′-nitrodiphenyl, 796·2 cm.$^{-1}$; 2-bromo-4′-nitrodiphenyl, 769 cm.$^{-1}$; 3-bromo-4′-nitrodiphenyl, 793·6 cm.$^{-1}$; 3-chlorodiphenyl, 795 cm.$^{-1}$; 4-chlorodiphenyl, 839 cm.$^{-1}$. The amounts of 4-chloro-4′-nitrodiphenyl, 4-bromo-4′-nitrodiphenyl,

and 2-chlorodiphenyl present in mixtures containing them were obtained by difference. In order to check the accuracy of the analyses, synthetic mixtures of chloro-4′-nitrodiphenyls, bromo-4′-nitrodiphenyls, and chlorodiphenyls of known composition were made up and analysed spectroscopically. The compositions found by analysis are compared with the known compositions in Table 3.

The results obtained in the analysis of the mixtures of isomers obtained in experiments 1—6 are given in Tables 2 and 4.

TABLE 3. *Analysis of synthetic mixtures.*

	Known compositions (%)			Compositions found from spectra (%)		
Mixture	2-	3-	4-	2-	3-	4-
S_1 (Chloro-4′-nitrodiphenyls)	54·2	24·1	21·7	55·3	24·8	19·9
S_2 (Bromo-4′-nitrodiphenyls)	48·0	26·1	25·9	50·1	27·2	22·7
S_3 (Bromo-4′-nitrodiphenyls	55·9	28·5	15·6	58·1	28·9	13·0
S_4 (Chlorodiphenyls)	54·7	30·0	15·3	55·0	29·1	15·9

TABLE 4. *Analysis of mixtures of isomeric halogeno-4′-nitrodiphenyls obtained in the p-nitrophenylation of chloro- and bromo-benzene* (PhX).

		Composition of halogeno-4′-nitrodiphenyls (%)		
Experiments	X in PhX	2 : 4′-	3 : 4′-	4 : 4′-
3	Cl	60·2	24·3	15·5
4	Cl	59·1	24·0	16·9
Mean	—	59·6	24·2	16·2
5	Br	60·0	25·5	14·5
6	Br	61·0	24·7	14·3
Mean	—	60·5	25·1	14·4

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528. *The Chemistry of Triterpenes and Related Compounds. Part XXXIII.* The Isolation of Ergosta-7 : 22-dien-3-one from* Fomes fomentarius.

By H. R. ARTHUR, T. G. HALSALL, and R. D. SMITH.

A simple steroid ketone, ergosta-7 : 22-diene-3-one, has been isolated from *Fomes fomentarius*.

IN continuation of our investigation of the wood-rotting fungi we have examined *Fomes fomentarius*, a large perennial fungus found in the British Isles only in the north of Scotland. Extraction of the fungus with light petroleum gave about 0·75% of a yellow paste which was separated by chromatography into two main fractions eluted with benzene and ether–methanol. The former yielded a ketone whose analysis indicated that it was either a steroid or triterpene containing 28 or 29 carbon atoms and no oxygen other that in the keto-group. Reduction with sodium borohydride gave two alcohols. Ozonolysis of the lower-melting alcohol gave 2 : 3-dimethylbutyraldehyde; on hydrogenation in acetic acid this alcohol absorbed one mol. of hydrogen but the intensity of the low-wavelength ultraviolet absorption of the product was greater than that of the starting material, indicating that a second double bond was being isomerised. These results suggested that the ketone and alcohols were ergosta-7 : 22-diene derivatives, the 7 : 8-double bond

* Part XXXII, *Croat. Chem. Acta*, 1957, **29**, 176.

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isomerising to the 8 : 14-position during hydrogenation.[1] Comparison of the constants of the ketone and the alcohols with those of ergosta-7 : 22-dien-3-one and the derived 3α- and 3β-alcohols (see Table), and direct comparison of the ketone and 3β-alcohol, proved the identity of the ketone.

This is the first time to our knowledge that a simple steroid ketone, as distinct from a triterpene, has been isolated from a natural source. Ergosta-7 : 22-dien-3β-ol has been isolated from Spanish grape-seed oil[3] and occurs as one of the minor sterols of yeast.[2]

	Found		Recorded	
	M. p.	$[\alpha]_D$	M. p.	$[\alpha]_D$
Ergosta-7 : 22-dien-3-one	184—187°	+6	177°,[a] 184·5 [1]	+1·5°,[a] +2° [1]
Ergosta-7 : 22-dien-3β-ol	171—174	−22	176 [1]	−19; −20
acetate	179—181	−15	178—180 [1]	−19
Ergosta-7 : 22-dien-3α-ol	214—215	−9	215—216 [b]	−4·4
acetate	146—148	0	156 [b]	+4

[a] Bladon, Henbest, and Wood, *J.*, 1952, 2737. [b] Windaus, Dithmar, Murke, and Suckfüll, *Annalen*, 1931, **488**, 91.

Experimental

M. p.s were determined of a Kofler block and are corrected. Rotations were determined for $CHCl_3$ solutions at room temperature. The alumina used for chromatography was of activity I—II unless otherwise stated. Light petroleum refers to the fraction with b. p. 60—80°.

Extraction of Fomes fomentarius *with Light Petroleum.*—The fungus (8 kg.) was cut into small pieces and extracted with light petroleum (30 l.) at 20° for three days. The extract was filtered and evaporated under reduced pressure, to give a yellow paste (60 g.). This was chromatographed on alumina (1 kg.), elution with benzene giving a white solid (20 g.) and elution with ether–methanol (9 : 1) a yellow paste (20 g.). By a tedious combination of chromatography and crystallisation from acetone the former solid was divided into fractions: (i) m. p. 100—205° (2·5 g.) and (ii) needles (5·0 g.), m. p. 175—179° (from acetone), raised by further crystallisation to 184—187°, $[\alpha]_D$ +6° (Found: C, 84·75; H, 11·3. Calc. for $C_{28}H_{44}O$: C, 84·8; H, 11·2%), $\nu_{max.}$ 1710 cm.$^{-1}$.

Reduction of the Ketone.—The ketone of m. p. 175—179° (0·512 g.) in dioxan–methanol (2 : 1, 30 ml.) was treated with sodium borohydride (0·3 g.) at 50° for 2 hr. Dilution with water and acidification with dilute sulphuric acid afforded a solid (0·52 g.) which was adsorbed from light petroleum on alumina (activity III; 50 g.). Elution with light petroleum–benzene (1 : 1; 350 c.c.) gave a solid (0·045 g.) which crystallised from acetone as needles, m. p. 201—205°, $[\alpha]_D$ −7°. After further elution with light petroleum–benzene (1 : 1; 150 c.c.) and benzene (300 c.c.), elution with benzene–ether (10 : 1; 200 c.c.; and 4 : 1; 700 c.c.) gave a solid (0·46 g.) which crystallised from acetone as prisms, m. p. 171—174°, $[\alpha]_D$ −22°. The infrared spectra indicated that both were alcohols. The two alcohols were more conveniently obtained directly from the benzene-eluted fraction resulting from chromatography of the light petroleum extract of the fungus. The fraction (1·0 g.) was dissolved in dioxan (20 c.c.) and methanol (10 c.c.). Sodium borohydride (1·0 g.) in dioxan (10 c.c.) and methanol (10 c.c.) was added and the mixture was boiled under reflux for 1 hr., then kept at *ca.* 40° for 3 hr. Most of the solvent was removed under reduced pressure, and water and dilute sulphuric acid were added. The white precipitate was collected, washed, and dried. It was adsorbed from light petroleum–benzene (2 : 1; 150 c.c.) on alumina (65 g.) deactivated with 5% of 10% aqueous acetic acid. Elution with light petroleum–benzene (1 : 1; 300 c.c.) gave only traces of oil and wax. After further elution with benzene (300 c.c.), benzene–ether (99 : 1; 400 c.c.) gave a fraction (0·055 g.) which crystallised from benzene and from acetone as needles, m. p. 214—215°, $[\alpha]_D$ −9° (Found: C, 84·5; H, 11·4. Calc. for $C_{28}H_{46}O$: C, 84·35; H, 11·65%). Acetylation gave the acetate which crystallised from acetone as prisms, m. p. 146—148°, $[\alpha]_D$ ±0° (Found: C, 81·6; H, 11·1. Calc. for $C_{30}H_{48}O_2$: C, 81·75; H, 11·0%). After further elution with benzene–ether (99 : 1; 450 c.c.), benzene–ether (9 : 1; 150 c.c.) gave a fraction (0·314 g.) which crystallised

[1] Barton and Cox, *J.*, 1948, 1354; Fieser and Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, 1949, p. 243.

[2] Elsevier's "Encyclopaedia of Organic Chemistry," 1954, Vol. XIV, Suppl., p. 1758 S; Wieland, Rath, and Hesse, *Annalen*, 1941, **548**, 34; Barton and Cox, *J.*, 1948, 1357.

[3] See ref. *a* of Table.

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from benzene and from acetone as prisms, m. p. 171—174°, $[\alpha]_D$ −22°. Acetylation gave the acetate, plates (from acetone), m. p. 179—181°, $[\alpha]_D$ −15°.

Ozonolysis of the Alcohol of m. p. 171—174°.—Ozonised oxygen was passed for 30 min. through a solution of the alcohol (500 mg.) in chloroform (50 ml.), and then the mixture was steam-distilled. The distillate was collected in aqueous dimedone solution, and this was then distilled with steam. The distillate was collected in a solution of 2 : 4-dinitrophenylhydrazine (400 mg.) in methanol (40 ml.) and sulphuric acid (0·25 ml.), and the resulting mixture was extracted with chloroform. The residue obtained after distillation of the chloroform was extracted with benzene. Evaporation of the benzene solution yielded an orange solid (65 mg.) which, after chromatography in benzene over alumina and crystallisation from methanol, gave 2 : 3-dimethylbutyraldehyde 2 : 4-dinitrophenylhydrazone as needles, m. p. and mixed m. p. 126—127°.

Hydrogenation of the Acetate of the Alcohol of m. p. 171—174°.—The acetate (0·150 g.; light absorption in *cyclo*hexane: ε_{2130} 3150; ε_{2150} 3000; ε_{2200} 1350; ε_{2230} 710) in chloroform (10 c.c.) and acetic acid (30 c.c.) was added to pre-reduced Adams catalyst (80 mg.) in acetic acid (10 c.c.) and hydrogenated at atmospheric pressure; ~1 mol. of hydrogen was taken up. After removal of catalyst, evaporation under reduced pressure gave a glass which crystallised from acetone as plates, m. p. 105—110°, light absorption in *cyclo*hexane: ε_{2130} 5530; ε_{2150} 5270; ε_{2200} 3850; ε_{2230} 2780.

Ergosta-7 : 22-*dien*-3β-*yl Acetate*.—This was prepared by Barton and Cox's method [1] and crystallised from methanol as plates, m. p. 177—179° (undepressed on admixture with the acetate of the alcohol of m. p. 171—174°), $[\alpha]_D$ −22°. The acetate (2·5 g.) was suspended in ether (100 c.c.), lithium aluminium hydride (0·5 g.) added, and the mixture heated under reflux for 2 hr. After addition of methanol and sulphuric acid ether-extraction afforded ergosta-7 : 22-dien-3β-ol, plates (from acetone), m. p. 175·5—176·5°, undepressed on admixture with the alcohol of m. p. 171—174°.

Ergosta-7 : 22-*dien*-3-*one*.[1,3]—Ergosta-7 : 22-dien-3β-ol (1·52 g.) in acetone (200 c.c.) was titrated with chromic acid solution as described by Bowers *et al.*[4] The product (1·4 g.), m. p. 165—166°, was adsorbed from light petroleum on alumina (activity I—II) which had been deactivated with 5% of 10% acetic acid. Elution with benzene–light petroleum (1 : 9) gave ergosta-7 : 22-dien-3-one (0·8 g.), needles (from acetone), m. p. 183—185° (undepressed on admixture with the ketone of m. p. 184—187° obtained from *Fomes fomentarius*), $[\alpha]_D$ +1°.

The authors thank Dr. D. G. Downie (University of Aberdeen) and Dr. J. A. MacDonald (University of St. Andrews) for generous assistance in collecting the fungus, and Dr. A. L. Lemin for preliminary work on its extraction. They also thank Professor E. R. H. Jones for his interest and advice. One of them (R. D. S.) thanks the United States Public Health Service for a Fellowship and another (H. R. A.) the University of Hong Kong for leave of absence.

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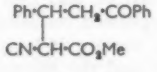
[4] Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2555.

529. *Chalcones and Related Compounds. Part VI.* Addition of Cyanoacetic Esters to Chalcones.*

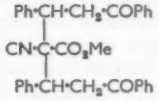
By W. Davey and D. J. Tivey.

Diethylamine is the preferred catalyst for the addition of cyanoacetic esters to chalcones. Hydrogenation of the benzyl cyanoacetate adducts yields 3 : 5-diaryl-2-cyano-5-oxopentanoic acids. Hydrogenation of ethyl 2-cyano-3 : 5-di-(*p*-methoxyphenyl)-5-oxopentanoate over Raney nickel W7 gives two isomeric tetrahydropyridines, which have been separated, and structures have been assigned to them.

Kohler, Graustein, and Merrill [1] have shown that, in presence of a small amount of sodium methoxide, methyl cyanoacetate added to chalcone, to give 2-cyano-5-oxo-3 : 5-diphenylpentanoate (I), together with the product of reaction of the primary adduct (I) and a second molecule of chalcone. By the use of the minimum quantity of sodium methoxide and effecting reaction in absolutely dry methanol, these workers limited the formation of the diadduct (II). We found addition of methyl or ethyl cyanoacetate to



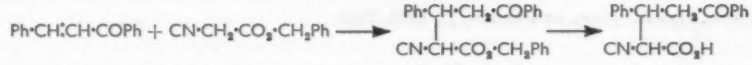
(I)



(II)

chalcones by this method to be difficult and to give variable results, so that other basic catalysts were investigated. Ammonia gave incomplete reaction but diethylamine gave reproducible results and the adducts obtained were free from biscondensation products. Although these adducts tended to separate as oils, crystallisation was achieved by extraction with benzene and drying.[2] Our attempts to hydrolyse the adducts by alkali failed, as did acid hydrolysis, *e.g.*, by Bowman's [3] or Bowman and Fordham's method.[4]

Attempts to effect ester interchange between benzyl alcohol and the methyl cyanoacetate adducts failed, and addition of benzyl cyanoacetate in ethanol to chalcone, in presence of diethylamine, followed by attempted hydrogenation, gave ethyl 2-cyano-5-oxo-3 : 5-diphenylpentanoate, ester interchange occurring during the addition. Addition of benzyl cyanoacetate in benzyl alcohol gave an oil, which on hydrogenation in ethyl methyl ketone in presence of palladium–charcoal, gave the required acid. This series of reactions was also carried out with 4 : 4′-dimethoxychalcone and appears to be a general route for the preparation of these hitherto inaccessible cyano-keto-acids.

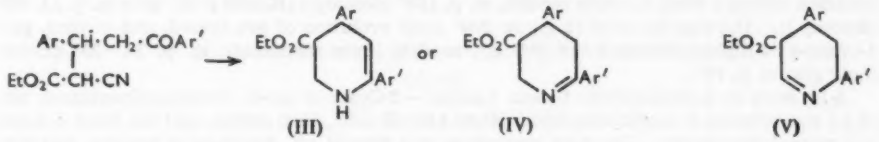


Three tetrahydropyridines are possible and, whilst derivatives of all three are known, only the Δ^3-isomer has been made with certainty. These isomers, obtained on reduction of pyridine with sodium and ethanol, cannot be separated by distillation.[5] Gabriel [6] has described the preparation of 1 : 2 : 3 : 4-tetrahydro-6-propylpyridine and advanced evidence for its structure, and Lipp [7] has described the methyl analogue. Reduction and cyclisation of 3 : 5-diaryl-2-cyano-5-oxopentanoic acids or their esters should give tetrahydropyridines. Compound (III) would be formed by elimination of water from the

* Part V, *J.*, 1958, 2276.

[1] Kohler, Graustein, and Merrill, *J. Amer. Chem. Soc.*, 1922, **44**, 2540.
[2] Davey and Tivey, *J.*, 1958, 2276.
[3] Bowman, *J.*, 1950, 322.
[4] Bowman and Fordham, *J.*, 1952, 3946.
[5] Koenigs and Bernhart, *Ber.*, 1905, **38**, 3042, 3928; 1907, **40**, 3199.
[6] Gabriel, *Ber.*, 1908, **41**, 2010; 1909, **42**, 1242, 4059.
[7] Lipp, *Ber.*, 1885, **18**, 3284.

enolic form of the ketone, whilst (IV) would be formed from the keto-form. Reduction of ethyl 2-cyano-3 : 5-di-(*p*-methoxyphenyl)-5-oxopentanoate catalytically in ethanol with Raney nickel W7 gave an oil, from which two pure picrates were obtained, giving the expected analyses. Regeneration of the bases, one crystalline and the other an oil, also gave satisfactory and identical analyses. Measurements of the pK values of the two bases gave very similar results (2·5—3·0) suggesting that both of these weak bases were Δ^1-compounds. Structures with the double bond in other positions should give higher pK values as secondary, and not tertiary, bases; *e.g.*, Adams and Mahan [8] found that 1-ethyl-1 : 2 : 3 : 4-tetrahydro-6-methyl- and 1 : 2 : 3 : 4-tetrahydro-6-methyl-pyridine gave pK values of 11·6 and 9·6 respectively. One of our bases had infrared bands at 1731



(ester C=O) and 1640 (CN), and aromatic bands at 1605 and 1512 cm.$^{-1}$, suggesting formula (V). The spectrum of the other base showed an ester-carbonyl band at 1715 cm.$^{-1}$, aromatic bands at 1591 and 1517 cm.$^{-1}$, and a band at 1609 cm.$^{-1}$ for the CN group conjugated with the aromatic system, indicating formula (IV; Ar = Ar′ = *p*-C_6H_4·OMe).

The conversion of 3 : 5-diaryl-2-cyano-5-oxopentanoic acids into lactones met with only a limited success.

Experimental

Addition of Ethyl Cyanoacetate to Chalcone.—Dropwise addition of sodium ethoxide solution to chalcone (20·8 g., 0·1 mole) and ethyl cyanoacetate (12·3 g., 0·11 mole) in dry ethanol (50 ml.) until the mixture was just alkaline to litmus raised the temperature almost to the b. p. and, after 1 hour's refluxing on a steam-bath and cooling in ice, crystals were obtained. Recrystallisation gave *ethyl 4-cyano-1 : 7-dioxo-1 : 3 : 5 : 7-tetraphenylheptane-4-carboxylate* as plates, m. p. 220—225° (decomp.) (19·0 g., 75%) (Found: C, 79·0; H, 5·6; N, 2·3. $C_{35}H_{31}O_4N$ requires C, 79·4; H, 5·9; N, 2·6%). Attempts to isolate the monoadduct were not successful.

Addition of Methyl Cyanoacetate to Chalcone.—Addition of methyl cyanoacetate (6·5 g., 0·063 mole) to chalcone (10·4 g., 0·05 mole) in methanol (25 ml.) in presence of sodium methoxide as above gave methyl 4-cyano-1 : 7-dioxo-1 : 3 : 5 : 7-tetraphenylheptane-4-carboxylate as plates, m. p. 223—225° (decomp.) (Kohler *et al.*[1] give m. p. 226°) (8·2 g.). Dilution of the methanol filtrate with water (11 ml.) gave an oil which was taken up in benzene (50 ml.); the benzene was removed *in vacuo*. The residual oil crystallised during 6 months and methyl 2-cyano-5-oxo-3 : 5-diphenylpentanoate (1·8 g.) was obtained as plates (from ether), m. p. 74—75° (Kohler *et al.*[1] give m. p. 76°).

Methyl 2-Cyano-5-oxo-3 : 5-diphenylpentanoate (I).—Addition of diethylamine (2 ml.) to chalcone (20·8 g., 0·1 mole) and methyl cyanoacetate (10·5 g., 0·11 mole) in dry methanol (80 ml.) at 50° caused a rapid rise in the temperature to the b. p. and after 15 minutes' refluxing the whole was diluted with water (80 ml.) and cooled in ice. Extraction of the oil with benzene (2 × 100 ml.) and removal of the benzene as above gave the cyano-ketone (20 g., 67%), m. p. 69—70° (Kohler *et al.*[1] give m. p. 76°).

Treatment of this ester with methanolic potassium hydroxide (Kohler *et al.*[1]) gave the diadduct (II) and only a trace of acid; heating the ester with sulphuric–acetic acid failed to achieve hydrolysis.

Benzyl Cyanoacetate.—(*a*) Slow distillation of ethyl cyanoacetate (56 g.), benzyl alcohol (54 g.), benzene (500 ml.), and sodium (0·5 g.) and fractionation under reduced pressure gave benzyl cyanoacetate (80 g., 92%), b. p. 130—135°/0·1 mm. (*b*) Benzyl alcohol (54 g.) with cyanoacetic acid (42·5 g.) in benzene (500 ml.) and sulphuric acid (0·5 ml.; *d* 1·84) gave benzyl cyanoacetate (72 g., 82%), b. p. 138—140°/1 mm. Newman and Magerlein [9] give b. p. 134—136°/0·5 mm.

[8] Adams and Mahan, *J. Amer. Chem. Soc.*, 1942, **64**, 2588.
[9] Newman and Magerlein, *ibid.*, 1946, **68**, 2112.

Addition of Benzyl Cyanoacetate to Chalcone.—Addition of diethylamine (2 ml.) to benzyl cyanoacetate (22 g., 0·13 mole) and chalcone (25 g., 0·12 mole) in ethanol (250 ml.) gave an oil, which was hydrogenated in ethanol (120 ml.) over 10% palladium–charcoal (2 g.). The oily product was *ethyl 2-cyano-5-oxo-3 : 5-diphenylpentanoate* (Found: C, 74·5; H, 5·7; N, 4·0. $C_{26}H_{19}O_3N$ requires C, 74·8; H, 5·9; N, 4·4%). Hydrogenation of the oil in ethyl methyl ketone gave the same product.

2-Cyano-5-oxo-3 : 5-diphenylpentanoic Acid.—Addition of benzyl cyanoacetate (22 g.) to chalcone (25 g., 0·12 mol.) in benzyl alcohol (100 ml.) at 90° with diethylamine (2 ml.) as catalyst, gave oily *benzyl 2-cyano-5-oxo-3 : 5-diphenylpentanoate* (Found: C, 77·5; H, 5·0; N, 4·2. $C_{25}H_{21}O_3N$ requires C, 78·3; H, 5·5; N, 3·7%) (44·6 g.). Hydrogenation in ethyl methyl ketone in presence of 10% palladium–charcoal (2 g.) then yielded an oil (30 g., 84%) which solidified during a week to white needles, m. p. 155° (decomp.) [Kohler *et al.*[1] give m. p. *ca.* 160° (decomp.)]. Heating the acid (2 g.) at 200° until evolution of gas ceased, and cooling, gave 4-cyano-1 : 3-diphenylbutan-1-one (0·7 g.), needles (from methanol), m. p. 74—75° (Kohler *et al.*[1] give m. p. 76°).

5-Hydroxy-3 : 5-diphenylpent-4-enoic Lactone.—2-Cyano-5-oxo-3 : 5-diphenylpentanoic acid (8 g.) was refluxed in acetic anhydride (20 ml.) for 30 min., then cooled, and the black solution was poured into water. The dark precipitate was filtered off, dissolved in benzene and light petroleum (b. p. 60—80°), and chromatographed on alumina. Elution gave an oil which slowly crystallised. 5-Hydroxy-3 : 5-diphenylpent-4-enoic lactone was obtained as needles, m. p. 140—160° (1·3 g.), after three crystallisation from ethanol (Found: C, 81·3; H, 5·5. Calc. for $C_{17}H_{14}O_2$: C, 81·6; H, 5·6%). Vorländer and Knotzsch [10] record no m. p. for this compound. Reduction of 2-cyano-5-oxo-3 : 5-diphenylpentanoic acid (5 g.) with potassium borohydride (1·5 g.) in 1 : 9 aqueous ethanol (40 ml.) at room temperature yielded an oil from which no solid lactone could be isolated.

Addition of Ethyl Cyanoacetate to 4 : 4′-Dimethoxy- and to 4-Hydroxy-chalcone.—Addition of ethyl cyanoacetate (12 g., 0·11 mole) to 4 : 4′-dimethoxychalcone (26 g., 0·1 mole) in ethanol (80 ml.) with diethylamine (2 ml.) at 50°, followed by 15 minutes' refluxing, dilution with water, and benzene-extraction, gave a viscous mass which crystallised from ethanol as plates, m. p. 115—116°, of *ethyl 2-cyano-3 : 5-di-(p-methoxyphenyl)-5-oxopentanoate* (28 g., 74%) (Found: C, 69·0; H, 5·9; N, 3·8. $C_{22}H_{23}O_5N$ requires C, 69·2; H, 6·1; N, 3·7%). The *adduct* from 4-hydroxychalcone was obtained as an oil (Found: C, 70·4; H, 6·2; N, 3·7. $C_{20}H_{19}O_4N$ requires C, 71·2; H, 5·6; N, 4·2%).

Addition of Benzyl Cyanoacetate to 4 : 4′-Dimethoxychalcone.—Benzyl cyanoacetate (13·4 g.) and 4 : 4′-dimethoxychalcone (10·4 g.) in ethanol (50 ml.) at 50° with diethylamine (2 ml.) as above gave ethyl 2-cyano-3 : 5-di-(*p*-methoxyphenyl)-5-oxopentanoate, m. p. and mixed m. p. 115—116° (15 g., 78%). Addition of benzyl cyanoacetate (27 g.) to 4 : 4′-dimethoxychalcone (13·4 g.) in benzyl alcohol (60 ml.) with diethylamine (3 ml.) at 90° gave an oil (23 g.) (Found: C, 72·7; H, 5·8; N, 3·0. Calc. for $C_{27}H_{25}O_5N$: C, 73·1; H, 5·7; N, 3·2%). Hydrogenation in ethyl methyl ketone with palladium–charcoal as before gave *2-cyano-3 : 5-di-(p-methoxyphenyl)-5-oxopentanoic acid* as needles (from benzene), m. p. 175—180° (decomp.) (Found: C, 67·5; H, 5·1; N, 4·2. $C_{20}H_{19}O_5N$ requires C, 68·0; H, 5·4; N, 4·0%).

5-Hydroxy-3 : 5-di-(p-methoxyphenyl)pentenoic Lactone.—Refluxing 2-cyano-3 : 5-di-(*p*-methoxyphenyl)-5-oxopentanoic acid (10 g.) with acetic anhydride (25 ml.) for 30 min. gave a dark solution which, when cooled and poured into water, afforded a dark semi-solid material. Chromatography on alumina as before gave the *lactone*, m. p. 128—130° (0·6 g.) (Found: C, 74·0; H, 5·6. $C_{18}H_{18}O_4$ requires C, 73·6; H, 5·8%).

Ethyl Tetrahydro-2 : 4-di-(p-methoxyphenyl)pyridinecarboxylate Isomers.—Ethyl 2-cyano-3 : 5-di-(*p*-methoxyphenyl)-5-oxopentanoate (10 g., 0·026 mole) in ethanol (60 ml.) was hydrogenated in presence of Raney nickel W7 (2 g.), hydrogen uptake corresponding to that required to convert the cyano- into an aminomethyl group. After filtration and evaporation of the filtrate *in vacuo*, a syrup (9 g.) was obtained. This was treated in ether (50 ml.) with picric acid (7 g.) in ether (50 ml.) and the yellow precipitate (11 g.; m. p. 160—180°) filtered off and fractionally crystallised from ethanol and then from benzene, giving the *picrate* of base A as yellow needles, m. p. 176—177° (1·7 g.) (Found: C, 56·6; H, 4·4; N, 9·2. $C_{28}H_{28}O_{11}N_4$ requires C, 56·3; H, 4·7; N, 9·4%), and the *picrate* of base B as yellow needles, m. p. 192—193° (2·5 g.) (Found: C, 56·5; H, 4·9; N, 9·3%). The former with 2N-sodium hydroxide (70 ml.) and

[10] Vorländer and Knotzsch, *Annalen*, 1897, **294**, 333.

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benzene (100 ml.) gave an oil, which crystallised from light petroleum (b. p. 40—60°) as isomer A, *ethyl* 1 : 2 : 3 : 4-*tetrahydro*-2 : 4-*di*-(p-*methoxyphenyl*)*pyridine*-5-*carboxylate*, needles, m. p. 117—118° (0·4 g.) (Found: C, 71·9; H, 6·8; N, 3·7. $C_{22}H_{25}O_4N$ requires C, 71·8; H, 6·8; N, 3·8%). The other picrate gave isomer B, *ethyl* 1 : 2 : 3 : 4-*tetrahydro*-4 : 6-*di*-(p-*methoxyphenyl*)-*pyridine*-3-*carboxylate*, an oil (Found: C, 71·3; H, 6·4; N, 3·5%). Attempts to hydrogenate both isomers in presence of Raney nickel W7 or platinic oxide were not successful.

We are grateful to Miss E. M. Tanner, Parke Davis & Co., Hounslow, Middlesex, for determinations of the infrared spectra and for suggestions on their interpretation.

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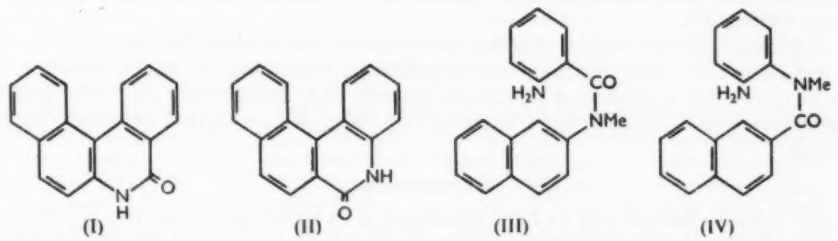
530. *The Ring-expansion of* 3 : 4-*Benzofluorenone by Hydrazoic Acid.*

By B. R. T. KEENE and K. SCHOFIELD.

3 : 4-Benzofluorenone is converted by hydrazoic acid into a mixture of 3 : 4- and 5 : 6-benzophenanthridone in which the former predominates. The derived *N*-methyl-3 : 4- and -5 : 6-benzophenanthridone differ from products, derived from Pschorr reactions, to which these structures were formerly attributed.

RING expansion of 3 : 4-benzofluorenone by means of the Schmidt reaction would be expected to give a mixture of 3 : 4- (I) and 5 : 6-benzophenanthridone (II). Available data[1] do not make possible a reliable prediction as to which of these products would predominate, and the reaction has now been examined since it might have provided a not too difficult means of obtaining 5 : 6-benzophenanthridine.[2]

When treated in cold concentrated sulphuric acid with sodium azide, 3 : 4-benzofluorenone appeared to suffer little change apart from some sulphonation. However, ring-expansion occurred in warm trichloroacetic acid containing a small amount of sulphuric acid,[3] the best yield [35—40% of a mixture of (I) and (II)] being obtained with



two equivalents of sodium azide. Separation of the isomers (I) and (II) proved difficult, but fractional dissolution in benzene left (II) undissolved and it could then be purified by recrystallisation. The isomer (I) was not obtained pure; sharp-melting specimens from recrystallisation always contained 5—10% of (II). Consequently, only a rough estimate of the ratio (2 : 1) of (I) to (II) in the product could be made. (On attempted chromatography on alumina the products could not be eluted.)

The structure of 5 : 6-benzophenanthridone (II) was proved by reduction with a considerable excess of lithium aluminium hydride[4] followed by dehydrogenation, which

[1] Arcus, Coombs, and Evans, *J.*, 1956, 1498.
[2] Mills and Schofield, *J.*, 1956, 4213.
[3] Smith, *J. Amer. Chem. Soc.*, 1948, **70**, 320.
[4] de Mayo and Rigby, *Nature*, 1950, **166**, 1075; Badger, Seidler, and Thomson, *J.*, 1951, 3207.

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gave 5 : 6-benzophenanthridine, identified as its picrate.[2] With dimethyl sulphate in acetone and aqueous sodium hydroxide, the amide (II) gave *N*-methyl-5 : 6-benzophenanthridone. That *N*-methylation had occurred was demonstrated by converting 5 : 6-benzophenanthridone into 9-chloro-5 : 6-benzophenanthridine, and thence into 9-methoxy-5 : 6-benzophenanthridine, which differed from the methylation product.

Attempts to convert the crude 3 : 4-benzophenanthridone (contaminated with a small proportion of the isomer) into 3 : 4-benzophenanthridine by the method described above gave a mixture of inseparable picrates. However, methylation of the impure 3 : 4-benzophenanthridone and fractional crystallisation of the product did give pure *N*-methyl-3 : 4-benzophenanthridone. This was identical with a specimen prepared by oxidising *N*-methyl-3 : 4-benzophenanthridinium iodide with alkaline potassium ferricyanide in aqueous dioxan.

Compounds thought to be *N*-methyl-3 : 4- and *N*-methyl-5 : 6-benzophenanthridone, m. p. 198—199° and 158—159° respectively, have been described in the literature. The first resulted [5] from the decomposition of the diazonium salt from *N*-*o*-aminobenzoyl-*N*-methyl-2-naphthylamine (III), and the second was obtained similarly [6] from *N*-methyl-*N*-β-naphthoyl-*o*-phenylenediamine (IV). Evidence for the structure of the compound, m. p. 198—199°, was its identity with a product obtained by oxidising *N*-methyl-3 : 4-benzophenanthridinium iodide with aqueous-methanolic alkaline potassium ferricyanide. The m. p. seems rather high for a compound of the supposed structure, and in carrying out the ferricyanide oxidation under slightly different conditions we isolated a product (m. p. 120—121°), mentioned above, which is clearly different from that described by the earlier workers. We cannot account for this discrepancy.

Evidence for the structure of the compound, m. p. 158—159°, formerly [6] taken to be *N*-methyl-5 : 6-benzophenanthridone, was the fact that it differed from the product obtained when 3-amino-*N*-methyl-2-naphthanilide was submitted to the Pschorr reaction. Abramovitch, Hey, and Long [6] found that decomposition of the diazonium salt from 1-amino-*N*-methyl-2-naphthanilide gave mainly 2-naphthanilide, together with two by-products, m. p. 137° and 185°, both differing from the compound, m. p. 158—159°, which they believed to be *N*-methyl-5 : 6-benzophenanthridone. The by-product, m. p. 137°, has now been found (infrared spectra) to be *N*-methyl-5 : 6-benzophenanthridone (m. p. 140—141°).

It is clear that the Pschorr-reaction products from the amides (III) and (IV) need to be re-formulated. Such reactions with naphthalene derivatives are clearly complex, and can be misleading in producing substances isomeric with, but different from, the expected phenanthridones. These Pschorr reactions are being re-investigated at King's College, London.

Experimental

The Schmidt Reaction with 3 : 4-*Benzofluorenone.*—3 : 4-Benzofluorenone (5·0 g.), trichloroacetic acid (100 g.), and concentrated sulphuric acid (5·0 g.) were kept at 55—65° and treated with powdered sodium azide (1·5 g.), added all at once. After the vigorous evolution of nitrogen had ceased (20 min.) more sodium azide (0·75 g.) was added, followed after 10 min. by a further quantity (0·5 g.). The reaction mixture was kept at 55—65° for 1 hr. more, then poured into iced water. After thorough extraction with chloroform, the organic layer was washed with dilute aqueous sodium carbonate and dried (Na_2SO_4). Evaporation left a dark brown tar which on trituration with benzene gave a buff powder (2·1 g., 39%), m. p. *ca.* 220—250°. This (2·1 g.) was heated under reflux with benzene (200 ml.) for 5 min. and the resulting suspension was filtered whilst hot. The insoluble portion (0·70 g.; m. p. 264—275°) was treated in the same way with a further quantity (50 ml.) of benzene, and the residue (0·65 g.) was crystallised from xylene, whence 5 : 6-*benzophenanthridone* formed yellow-bronze needles, m. p. 275—276° (Found: C, 83·6; H, 4·6. $C_{17}H_{11}ON$ requires C, 83·2; H, 4·5%). This

[5] Hey and Turpin, *J.*, 1954, 2471.
[6] Abramovitch, Hey, and Long, *J.*, 1957, 1781.

compound existed in two crystalline modifications. Slow crystallisation from a relatively large volume of xylene yielded clusters of yellow-bronze needles, whilst from a small volume of solvent the compound formed matted buff fibres. The two forms had identical m. p.s and by crystallisation from an intermediate volume of solvent mixtures of both were obtained.

The benzene-soluble fraction was isolated as a brown solid, m. p. 236—240° (1·23 g.). Two crystallisations from xylene yielded buff needles, m. p. 241—243°, consisting mainly of 3 : 4-benzophenanthridone (Found: C, 83·7; H, 4·0%).

5 : 6-*Benzophenanthridine.*—5 : 6-Benzophenanthridone (0·10 g.) in a Soxhlet thimble was extracted slowly into a boiling suspension of lithium aluminium hydride (0·10 g.) in tetrahydrofuran (50 ml.). When all the material had been removed from the thimble the mixture was heated under reflux for a further 1½ hr. After cooling, the excess of lithium aluminium hydride was decomposed by the addition of aqueous tetrahydrofuran. Most of the solvent was distilled off, and the residue was made alkaline with 10% aqueous sodium hydroxide (100 ml.) and thoroughly extracted with benzene. Evaporation of the dried ($MgSO_4$) extract left a yellow gum which was heated with 30% palladium–charcoal (0·10 g.) for 3 hr. at 280° in a stream of nitrogen. The cooled mixture was extracted with hot ethanol, and the filtered solution treated with picric acid (0·10 g.) in ethanol. The bright yellow picrate [(0·085 g.; m. p. 252—254° (decomp.)] so formed, crystallised from 2-ethoxyethanol as yellow fibres (Found: C, 60·5; H, 3·25; N, 11·9. Calc. for $C_{17}H_{11}N,C_6H_3O_7N_3$: C, 60·3; H, 3·1; N, 12·1%), m. p. 253—254° alone or mixed with 5 : 6-benzophenanthridine picrate.[2]

N-*Methyl*-5 : 6-*benzophenanthridone.*—5 : 6-Benzophenanthridone (0·20 g.), acetone (50 ml.), and 10% aqueous sodium hydroxide (5 ml.) were heated under reflux and treated slowly with dimethyl sulphate (0·50 g.). The solution (kept alkaline with dilute aqueous sodium hydroxide) was boiled for 30 min., then treated with a further quantity of dimethyl sulphate (0·50 g.), heated for 15 min., and poured into ice-water kept alkaline with dilute aqueous sodium hydroxide. Extraction with benzene and evaporation of the dried (Na_2SO_4) extract yielded N-*methyl*-5 : 6-*benzophenanthridone* (0·14 g.) as a buff solid, m. p. 132—135°, which formed white needles, m. p. 140—141° (Found: C, 83·9; H, 5·0; N, 5·6. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·05; N, 5·5%), from methanol.

The infrared spectrum of this compound was identical with that of the compound, m. p. 137°, described by Abramovitch, Hey, and Long.[6]

9-*Methoxy*-5 : 6-*benzophenanthridine.*—5 : 6-Benzophenanthridone (0·20 g.), phosphorus oxychloride (6 ml.), and dimethylaniline (0·50 ml.) were heated under reflux for 4 hr. Liquids were then removed at reduced pressure, the last traces being eliminated by the addition and evaporation of three successive quantities of benzene. The residue was treated with ice and water, and the mixture extracted with chloroform. Evaporation of the dried (Na_2SO_4) extract left a brown gum which on trituration with light petroleum (b. p. 40—60°) yielded 9-chloro-5 : 6-benzophenanthridine as a pink, gritty solid, m. p. 105—108° (0·17 g.).

The chloro-compound (0·17 g.) was heated under reflux with methanolic sodium methoxide [from sodium (0·23 g.) and methanol (10 ml.)] for 6 hr. After the methanol had been removed at reduced pressure, the residue was treated with ice and water and extracted with benzene. Evaporation of the dried (Na_2SO_4) extract left a brown oil which on trituration with methanol gave 9-*methoxy*-5 : 6-*benzophenanthridine* (0·08 g.; m. p. 73—75°) as a pink solid which formed clusters of ivory-coloured needles, m. p. 75—76° (Found: C, 83·7; H, 5·2; OMe, 12·2. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·05; OMe, 12·0%), from methanol.

N-*Methyl*-3 : 4-*benzophenanthridone.*—(i) Methylated under the conditions described above, impure 3 : 4-benzophenanthridone (0·40 g.) yielded a brown gum (0·35 g.). After traces of tar had been removed by passage in benzene over alumina the residue was triturated with methanol and a quantity of *N*-methyl-5 : 6-benzophenanthridone filtered off. Concentration of the mother-liquors at room temperature under reduced pressure yielded the crude product (0·15 g.), m. p. 92—99°. Two crystallisations from light petroleum (b. p. 60—80°) gave N-*methyl*-3 : 4-*benzophenanthridone* as white needles, m. p. 120—121° (Found: C, 83·75; H, 5·1; N, 5·4%).

(ii) 3 : 4-Benzophenanthridine [2] (0·4 g.) was heated under reflux with methyl iodide (1·24 g.) and absolute methanol (20 ml.) for 3 hr.; 3 : 4-benzophenanthridine methiodide separated as yellow crystals (0·40 g.). This (0·30 g.) in dioxan (7·5 ml.) and water (7·5 ml.) was treated with potassium hydroxide (0·40 g.) in water (1·2 ml.). Potassium ferricyanide (0·60 g.) in water (5 ml.) was added and the mixture was heated, with frequent shaking, for 30 min. on

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the water-bath. After dilution with water the precipitated material was extracted with ether. Evaporation of the dried (Na_2SO_4) extract left a yellow-green oil which on trituration with light petroleum yielded a white solid (0·11 g.), m. p. 114—118°. Crystallisation from light petroleum (b. p. 60—80°) gave *N*-methyl-3 : 4-benzophenanthridone as white needles, m. p. 120—121° alone or mixed with a specimen obtained as above. Both specimens exhibited the same slight blue fluorescence in ethanol.

We are grateful to Professor D. H. Hey and Drs. R. A. Abramovitch and R. Long for discussions, for kindly supplying specimens, and for determining the infrared spectrum of *N*-methyl-5 : 6-benzophenanthridone.

WASHINGTON SINGER LABORATORIES,
PRINCE OF WALES ROAD, EXETER. [*Received, February 21st*, 1958.]

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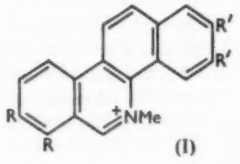
531. *Some Synthetical Investigations in* isoCoumarin *Chemistry.*

By J. B. JONES and A. R. PINDER.

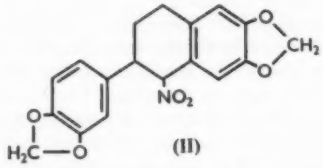
Preliminary experiments on possible new routes to the *Chelidonium* alkaloids are described, and syntheses of some derivatives of naphtho(1′ : 2′-3 : 4)*iso*coumarin are outlined.

DEGRADATIVE studies of chelerythrine (I; R = OMe, R′R′ = O_2CH_2) and sanguinarine (I; RR = R′R′ = O_2CH_2), two of the four principal alkaloids of *Chelidonium majus*, showed that the bases were derived from 1 : 2-benzophenanthridine.[1] The major contribution towards the synthesis of the alkaloids has been made by Robinson and his co-workers,[2] who have synthesised several compounds closely related to chelerythrine. These investigations recently culminated in a total synthesis of chelerythrine chloride.[3]

The object of the investigations described here, which were begun before the chelerythrine synthesis was announced, was to explore possible alternative routes to these alkaloids.



(I)



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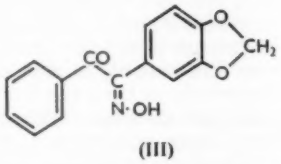


(III)

Recent studies of Diels–Alder type additions between ω-nitrostyrenes and buta-1 : 3-diene and its homologues [4] suggested that the compound (II), a possible intermediate in the synthesis of bases of type (I), might be formed by addition of 3 : 4-methylenedioxy-ω-nitrostyrene to 3 : 4-methylenedioxystyrene. Model experiments with ω-nitrostyrene and 3 : 4-methylenedioxystyrene were, however, discouraging. This failure, under a variety of conditions, recalls that of Hudson and Robinson,[5] who were unable to obtain a normal adduct from maleic anhydride and 3 : 4-methylenedioxystyrene, and is presumably explicable by the deactivating influence of the *p*-alkoxyl group on the double bond in the latter.

The observation that ω-hydroxyiminoacetophenone and benzenediazonium chloride condense to form benzil monoxime [6] suggested that possible intermediates such as (III)

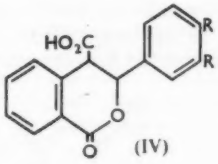
[1] Henry, "The Plant Alkaloids," Churchill, London, 1949, p. 277; Manske and Holmes, "The Alkaloids," Academic Press, New York, 1954, Vol. IV, Chapter 35.
[2] Richardson, Robinson, and Seijo, *J.*, 1937, 835; Bailey and Robinson, *Nature*, 1949, **164**, 402; *J.*, 1950, 1375; Bailey, Robinson, and Staunton, *Nature*, 1950, **165**, 235; *J.*, 1950, 2277.
[3] Bailey and Worthing, *J.*, 1956, 4535.
[4] Wildman and Wildman, *J. Org. Chem.*, 1952, **17**, 581; Mason and Wildman, *J. Amer. Chem. Soc.*, 1954, **76**, 6194.
[5] Hudson and Robinson, *J.*, 1941, 715.
[6] Kanno, *J. Pharm. Soc. Japan*, 1953, **73**, 118.

were derivable by an analogous condensation, but attempts to condense ω-hydroxyiminoacetophenone with 3 : 4-methylenedioxybenzenediazonium chloride were unsuccessful.

The reaction of *iso*coumarins with ammonia or a primary amine to give *iso*quinolones [7] (*iso*carbostyrils), and the conversion of other lactones into lactams under similar conditions,[8] are well-known transformations, and it seemed that a more profitable route to the benzophenanthridine bases might be *via* a naphtho*iso*coumarin.

Müller's observation [9] that the sodium enolate of homophthalic anhydride and benzaldehyde condense to form the dihydro*iso*coumarin (IV; R = H) appeared an interesting starting point. We have repeated this condensation and found the properties and infrared absorption of the product to be in agreement with this formula assigned to it by Müller. When benzaldehyde was replaced by piperonaldehyde in this condensation, the product was the analogue (IV; RR = O_2CH_2): and if condensation is effected with sodamide in liquid ammonia isolation of the sodium enolate and the long reaction period are obviated.

Loewenthal and Pappo [10] have obtained the acid (IV; R = H) by a Stobbe-type condensation between benzaldehyde and dimethyl homophthalate, the product being cyclised with hydrobromic–acetic acids. We have condensed piperonaldehyde with the same ester and obtained methyl α-*o*-carboxyphenyl-3 : 4-methylenedioxycinnamate (V; R = Me), but attempts to cyclise this compound or the corresponding dicarboxylic acid (V; R = H) led to extensive decomposition, presumably because of the sensitivity of the methylenedioxy-group to acids. When the acid (V; R = H), m. p. 233°, was warmed with acetic anhydride it yielded an orange-yellow anhydride, m. p. 197°, presumably identical with the compound (m. p. 196°) obtained by Buu-Hoï [11] by the condensation of piperonaldehyde with homophthalic anhydride in the presence of piperidine. Inspection of molecular models shows that this compound must have the *cis*-configuration (VI); *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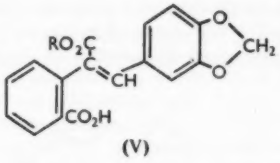
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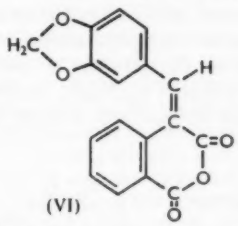
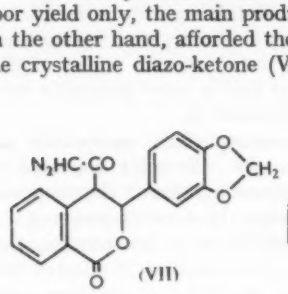

(VI)

in the corresponding *trans*-isomer there is considerable steric interference between the methylenedioxyphenyl group and the anhydride ring. Mild alkaline hydrolysis of the anhydride afforded an acid, m. p. 180°, isomeric with the original acid. The two acids appear to be geometrical isomers; models show that the hydrolysis of the anhydride ring removes the steric interference, both *cis*- and *trans*-forms of the acid (V; R = H) being stereochemically possible. In the ultraviolet spectrum the acid of m. p. 233° shows a principal maximum at 320 mμ, and the acid of m. p. 180° a much weaker one at 315 mμ. Generally, *trans*-compounds absorb at longer wavelengths and with greater intensity than their *cis*-isomers,[12] and on this evidence we assign the *trans*-configuration to the acid of m. p. 233° and the *cis* to the acid of m. p. 180°.

* The prefix *cis* is used to denote that the two benzene rings are on the same side of the plane of the double bond.

[7] Gabriel, *Ber.*, 1885, **18**, 2433, 3470; 1886, **19**, 830, 1653.
[8] Meyer, *Monatsh.*, 1899, **20**, 717; Späth and Lintner, *Ber.*, 1936, **69**, 2927; Wiley *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 4482; 1954, **76**, 625.
[9] Müller, *Annalen*, 1931, **491**, 251.
[10] Loewenthal and Pappo, *J.*, 1952, 4799.
[11] Buu-Hoï, *Compt. rend.*, 1940, **211**, 330, 563, 643.
[12] Gillam and Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Arnold, 1954, pp. 232—246; Braude, *J.*, 1949, 1902.

With thionyl chloride the lactonic acid (IV; RR = O_2CH_2) gave the acid chloride in poor yield only, the main product being the anhydride (VI). Phosphorus pentachloride, on the other hand, afforded the chloride in good yield. With diazomethane this yielded the crystalline diazo-ketone (VII), which was smoothly converted into the homologous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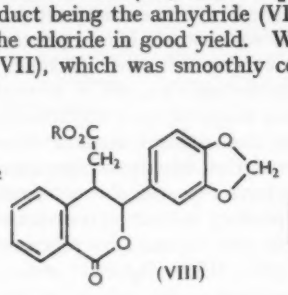
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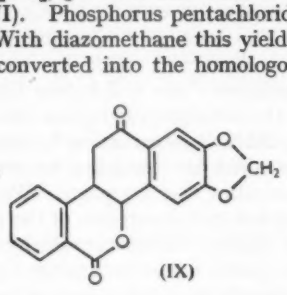
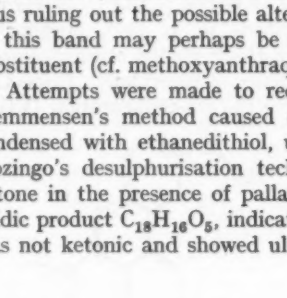

(IX)

methyl ester (VIII; R = Me) by silver benzoate in methanol containing triethylamine.[13] Hydrolysis gave the acid (VIII; R = H), which, in contrast to its lower homologue, yielded its chloride readily with thionyl chloride. Cyclisation of this with stannic chloride afforded the naphtho*iso*coumarin (IX). That the cyclisation had occurred in the expected direction (involving the reactive *para*-position of the methylenedioxybenzene ring) was proved by the presence of a strong band in the infrared absorption spectrum of the ketone at 1664 cm.$^{-1}$, characteristic of an αβ-unsaturated carbonyl group in a six-membered ring,[14a] thus ruling out the possible alternative structure (X). The somewhat low wave-number of this band may perhaps be accounted for by the influence of the methylenedioxy-substituent (cf. methoxyanthraquinones[14b]).

Attempts were made to reduce the ketone (IX) to the compound (XI; R = H). Clemmensen's method caused extensive decomposition and the ketone could not be condensed with ethanedithiol, under the usual conditions, to form a thioketal, so that Mozingo's desulphurisation technique[15] could not be applied. Hydrogenation of the ketone in the presence of palladium–charcoal promoted with perchloric acid[16] gave an acidic product $C_{18}H_{16}O_5$, indicating reductive cleavage of the lactone ring. This product was not ketonic and showed ultraviolet absorption similar to that of benzoic acid;[17] a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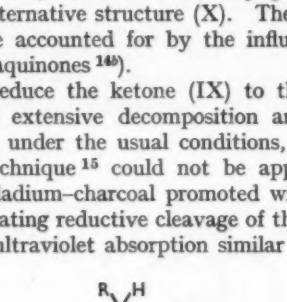
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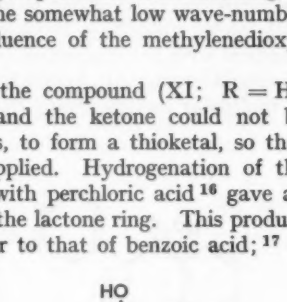
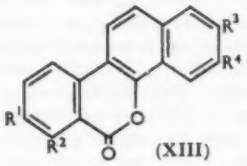

(XII)

hydroxyl band could not be detected in the infrared absorption curve, probably because the compound, which we formulate as (XII), is monomeric so that the alcoholic hydroxyl band is masked by a strong carboxyl band in the 3400 cm.$^{-1}$ region.

Reduction of the ketone (IX) with potassium borohydride afforded the alcohol (XI; R = OH), obtained in two modifications. Dehydrogenation of this compound resulted in the elimination of water and the formation of 6′ : 7′-methylenedioxynaphtho(1′ : 2′-3 : 4)*iso*coumarin (XIII; $R^1 = R^2 = H$, $R^3R^4 = O_2CH_2$), unfortunately in very poor yield, the structure of the product being confirmed by its chemical properties and infrared

[13] Cf. Newman and Beal, *J. Amer. Chem. Soc.*, 1950, **72**, 5163.
[14] (*a*) Cf. Grove and Willis, *J.*, 1951, 877; (*b*) Wiles and Thomas, *J.*, 1956, 4811.
[15] Mozingo *et al.*, *J. Amer. Chem. Soc.*, 1943, **65**, 1013, 1477.
[16] Cf. Rosenmund and Karg, *Ber.*, 1942, **75**, 1850; Kindler *et al.*, *ibid.*, 1943, **76**, 308; Baker and Jenkins, *J. Amer. Chem. Soc.*, 1946, **68**, 2102; Johnson and Graber, *ibid.*, 1950, **72**, 925.
[17] Ref. 12, p. 126.

absorption. The ultraviolet absorption curve was closely similar to that of the tetramethoxy-analogue synthesised by Bailey and Worthing.[3] An accompanying dehydrogenation product was a neutral compound $C_{18}H_{10}O_3$, which was not lactonic and showed ketonic properties. Its ultraviolet absorption curve resembled closely that of 3 : 4-benzofluorenone,[18] and the presence of a diaryl ketone grouping was indicated by the appearance



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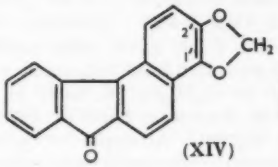
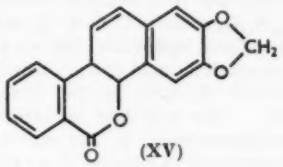


(XIV)



(XV)

in the infrared spectrum of a band at 1693 cm.$^{-1}$, the position of which is probably modified by the methylenedioxy-substituent.[14b,19] On these grounds structure (XIV) is proposed for the compound.

Treatment of the alcohol (XI; R = OH) with hydrogen chloride or phosphorus tribromide or pentachloride gave the anhydro-compound (XV), which showed no hydroxyl band in the infrared spectrum. Attempts to dehydrogenate this compound were equally discouraging, the same two products being obtained in very poor yield.

Experimental

Ultraviolet absorption spectra were determined on methanol solutions, and infrared spectra for Nujol mulls, unless otherwise stated.

4-Carboxy-3 : 4-dihydro-3-(3 : 4-methylenedioxyphenyl)isocoumarin (IV; RR = O_2CH_2).—(*a*) Homophthalic anhydride was prepared by dehydration of homophthalic acid,[20] obtained by oxidation of indene.[21] The anhydride (4·0 g.), in the minimum quantity of warm, dry benzene, was added dropwise with swirling to an ethereal 0·13M-solution of triphenylmethylsodium (690 c.c., 1 mol.) [22] under nitrogen. The yellow enolate was collected, washed with ether, suspended in dry ether (50 c.c.), and shaken with a solution of piperonaldehyde (7·5 g.) in dry ether (50 c.c.) under nitrogen at room temperature for 7 days.[23] Water (100 c.c.) was then added and the aqueous layer separated and acidified. The liberated *acid* was collected and crystallised from 50% acetic acid, from which it separated in rhombic prisms of the *monohydrate* (1·6 g.) (Found: C, 61·9; H, 4·1. $C_{17}H_{12}O_6,H_2O$ requires C, 61·8; H, 4·2%), which at 100° *in vacuo* gave the anhydrous *acid*, m. p. 180° (decomp.) (Found: C, 65·1; H, 4·0. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·9%), $\nu_{max.}$ 1704 (lactone-CO), 1735 (carboxyl-CO), and 3175 cm.$^{-1}$ (OH). With ethereal diazomethane the acid afforded the *methyl ester*, rhombic prisms (from methanol), m. p. 145—145·5° (Found: C, 66·2; H, 4·2. $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3%), $\nu_{max.}$ 1720 (lactone-CO) and 1730 cm.$^{-1}$ (ester CO) (no OH band).

(*b*) To liquid ammonia (600 c.c.) containing ferric nitrate (0·2 g.) sodium (2·4 g.; 1·05 atom.) was added gradually in small pieces, with stirring. When the metal had dissolved homophthalic anhydride (16·2 g., 1 mol.) in dry benzene (600 c.c.) was added dropwise, followed by piperonaldehyde (15 g.) in dry benzene (100 c.c.), with stirring throughout. Next morning water (200 c.c.) was added and the aqueous layer separated and acidified with 5N-hydrochloric acid. The liberated acid (22 g.) crystallised from 50% acetic acid as the monohydrate, which when dried at 100° *in vacuo* had m. p. 180° (decomp.) alone or mixed with the product obtained as in (*a*).

[18] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, 1951, curve 434.
[19] Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1954, pp. 114, 119; Jones and Sandorfy in "Techniques of Organic Chemistry," Interscience Publ. Inc., New York, 1956 Vol. IX, p. 450.
[20] Price, Lewis, and Meister, *J. Amer. Chem. Soc.*, 1939, **61**, 2762.
[21] Cooney and Whitmore, *ibid.*, 1944, **66**, 1237.
[22] "Organic Reactions," Vol. I, p. 286.
[23] Cf. Müller, *Annalen*, 1931, **491**, 260.

XUM

Methyl α-o-Carboxyphenyl-3 : 4-methylenedioxycinnamate (V; R = Me).[24]—Dimethyl homophthalate [25] (4·2 g.) in dry methanol (25 c.c.) was added gradually to a solution of sodium methoxide prepared by dissolving sodium (0·46 g.) in dry methanol (25 c.c.). Piperonaldehyde (3·0 g.) in dry methanol (15 c.c.) was then added and the mixture refluxed on the water-bath for 3 hr. The solvent was evaporated under reduced pressure and the residual syrup taken up in water (50 c.c.) and acidified with 5N-hydrochloric acid. The *acid* (6·3 g.) was collected and crystallised from benzene, in rhombic prisms, m. p. 173·5° (Found: C, 65·5; H, 4·5; OMe, 9·0. $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3; OMe, 9·5%). Hydrolysis of the product (3·3 g.) by refluxing 2N-sodium hydroxide (30 c.c.) for 2 hr. gave, after acidification, *trans*-α-piperonylidenehomophthalic acid (2·8 g.), which separated from 70% acetic acid in cubes, m. p. 233° (decomp.) (Found: C, 65·3; H, 3·8. Calc. for $C_{17}H_{12}O_6$: C, 65·4; H, 3·9%). Buu-Hoï [11] gives m. p. 235°. The acid had an infrared absorption band at 1678 cm.$^{-1}$ (CO) and an ultraviolet absorption max. at 320 mμ (ε 15,700). Attempts to cyclise both the above products to 4-carboxy-3 : 4-dihydro-3-(3 : 4-methylenedioxyphenyl)*iso*coumarin (IV; RR = O_2CH_2) by hydrobromic–acetic acids [10] led to extensive decomposition.

α-Piperonylidenehomophthalic Anhydride (VI).—The above dicarboxylic acid (0·3 g.) was refluxed for 30 min. with acetic anhydride (5 c.c.). The solution was evaporated to dryness *in vacuo*. The residual orange anhydride (0·17 g.) crystallised from benzene in feathery orange needles, m. p. 197° (Buu-Hoï [11] gives m. p. 196°) (Found: C, 69·7; H, 3·4. Calc. for $C_{17}H_{10}O_5$: C, 69·4; H, 3·4%). Hydrolysis of the anhydride (0·1 g.) by refluxing 2N-sodium hydroxide (10 c.c.) for 30 min. gave cis-*α-piperonylidenehomophthalic acid* (0·1 g.), which separated from 50% acetic acid in very pale yellow needles, m. p. 180° (decomp.) (Found: C, 65·6; H, 4·25. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·9%), $\lambda_{max.}$ 315 mμ (ε 10,300), $\nu_{max.}$ 1685 cm.$^{-1}$ (CO).

4-*Chlorocarbonyl*-3 : 4-*dihydro*-3-(3 : 4-*methylenedioxyphenyl*)iso*coumarin*.—The dry lactonic acid (IV; RR = O_2CH_2) (25 g.) and phosphorus pentachloride (20·8 g.) were mixed and kept at room temperature for 8 hr. Phosphorus oxychloride was removed *in vacuo* at room temperature and the residue crystallised from benzene, from which the *acid chloride* separated in rhombic prisms (17·7 g.), m. p. 141—142° (Found: C, 62·1; H, 3·6. $C_{17}H_{11}O_5Cl$ requires C, 61·7; H, 3·3%). When warmed with methanol the product afforded the corresponding methyl ester, m. p. 141—142°, alone or mixed with the ester obtained by the action of diazomethane on the parent acid (see above). With thionyl chloride the lactonic acid afforded mainly α-piperonylidenehomophthalic anhydride (see above).

4-*Diazoacetyl*-3 : 4-*dihydro*-3-(3 : 4-*methylenedioxyphenyl*)iso*coumarin* (VII).—The above acid chloride (17·6 g.) in dry benzene (240 c.c.) was added dropwise, with swirling, to a cooled solution of diazomethane (4·5 g.) in dry ether (160 c.c.).[26] After being kept overnight at 0° the crystalline *diazo-ketone* was collected (17·2 g.). A sample crystallised from dioxan–ether in rhombic prisms, m. p. 149° (decomp.) (Found: C, 64·5; H, 3·9. $C_{18}H_{12}O_5N_2$ requires C, 64·3; H, 3·6%).

4-*Methoxycarbonylmethyl*-3 : 4-*dihydro*-3-(3 : 4-*methylenedioxyphenyl*)iso*coumarin* (VIII; R = Me).—Dry silver benzoate (2·5 g.) in anhydrous triethylamine (50 c.c.) was filtered and added portionwise during 30 min. to the above diazo-ketone (11·2 g.) in dioxan–methanol (1 : 1; 400 c.c.) at room temperature, with shaking.[13] Nitrogen was evolved and the solution darkened. A little " Norit " was added and the solution boiled for 2 min.; it was then filtered and concentrated under reduced pressure. The residual gum was purified by chromatography in benzene–light petroleum (b. p. 40—60°) on alumina, with elution with benzene. Evaporation of the eluate afforded a syrup which solidified on trituration with methanol. The *ester* separated from methanol in feathery needles, m. p. 116° (6·7 g.) (Found: C, 67·6, 67·4; H, 4·9, 4·8. $C_{19}H_{14}O_6$ requires C, 67·1; H, 4·7%).

4-*Carboxymethyl*-3 : 4-*dihydro*-3-(3 : 4-*methylenedioxyphenyl*)iso*coumarin* (VIII; R = H).—(*a*) The foregoing methyl ester (3·4 g.) was refluxed for 30 min. with a mixture of glacial acetic acid, concentrated hydrochloric acid, and water (3 : 1 : 1 by vol.; 60 c.c.). The solution was cooled, diluted, and extracted with ether. The extract was washed several times with sodium hydrogen carbonate solution, and the combined aqueous layers were acidified with 5N-hydrochloric acid. The solid was collected, washed with water, and crystallised from 50% acetic acid. 4-*Carboxymethyl*-3 : 4-*dihydro*-3-(3 : 4-*methylenedioxyphenyl*)iso*coumarin*

[24] Cf. Loewenthal and Pappo, ref. 10; Dieckmann, *Ber.*, 1914, **47**, 1428.
[25] Sheehan and O'Neill, *J. Amer. Chem. Soc.*, 1950, **72**, 4614.
[26] *Org. Synth.*, 1935, **15**, 4.

separated in feathery needles, m. p. 172·5° (Found: C, 65·9, 66·1; H, 4·2, 4·65. $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3%), $\nu_{max.}$ 1678 (probably internally hydrogen-bonded carboxyl-carbonyl group) and 1724 cm.$^{-1}$ (lactone-carbonyl group).

(*b*) The same ester (0·6 g.) was refluxed for 2 hr. with 2N-sodium hydroxide (15 c.c.). Concentrated hydrochloric acid (5 c.c.) and glacial acetic acid (5 c.c.) were then added and the mixture refluxed for a further 30 min. The acid (0·5 g.), isolated by the same procedure as in (*a*), crystallised from 50% acetic acid in rhombic prisms, m. p. 163—164° (Found: C, 66·5; H, 4·4%). When a solution of this acid in 50% acetic acid was inoculated with a crystal of the acid of m. p. 172·5°, crystals of m. p. 172·5° were obtained. The infrared absorption spectra of the two acids were identical.

1′ : 2′ : 3′ : 4′-*Tetrahydro*-6′ : 7′-*methylenedioxy*-4′-*oxonaphtho*(1′ : 2′-3 : 4)iso*coumarin* (IX).—The above acid (3·25 g.), purified chloroform (60 c.c.), and purified thionyl chloride (2·4 g.) were refluxed on the water-bath for 45 min. Removal of the solvent and excess of thionyl chloride *in vacuo* gave a syrup which was dissolved in chloroform (100 c.c.), cooled, and treated with stannic chloride (5·2 g.), which was added dropwise at 0°, with shaking. After being kept overnight at this temperature the complex which had separated was decomposed with 5N-hydrochloric acid, and the chloroform layer separated, washed with dilute sodium hydroxide solution and water, dried, and evaporated. The crystalline *ketone* remaining separated from benzene or a large volume of ethanol in feathery needles, m. p. 229° (1·9 g.) (Found: C, 69·6; H, 4·0. $C_{18}H_{12}O_5$ requires C, 70·1; H, 3·9%), $\nu_{max.}$ 1502 and 1603 (aromatic ring conjugated with carbonyl group), 1664 (conjugated CO group in six-membered ring), and 1706 cm.$^{-1}$ (lactone-CO). The *semicarbazone* crystallised from ethanol in needles, m. p. 260—261° (decomp.) (Found: C, 62·7; H, 4·3. $C_{19}H_{15}O_5N_3$ requires C, 62·5; H, 4·1%). The 2 : 4-*dinitrophenylhydrazone* separated from nitrobenzene in orange needles, m. p. 305° (Found: N, 11·9. $C_{24}H_{16}O_8N_4$ requires N, 11·5%).

1′ : 2′ : 3′ : 4′-*Tetrahydro*-4′-*hydroxy*-6′ : 7′-*methylenedioxynaphtho*(1′ : 2′-3 : 4)iso*coumarin* (XI; R = OH).—A solution of potassium borohydride (0·14 g.) in 80% dioxan (25 c.c.) was mixed with the foregoing ketone (0·62 g.) in 80% dioxan (60 c.c.). After 1 hr. the solution was acidified with dilute sulphuric acid and poured into a large volume of water. The precipitate was collected and dried (0·56 g.); 1′ : 2′ : 3′ : 4′-*tetrahydro*-4′-*hydroxy*-6′ : 7′-*methylenedioxynaphtho*(1′ : 2′-3 : 4)iso*coumarin* separated from ethanol in prismatic needles, m. p. 167° (Found: C, 69·7; H, 4·5. $C_{18}H_{14}O_5$ requires C, 69·7; H, 4·5%), $\nu_{max.}$ 1703 (lactone-CO) and 3400 cm.$^{-1}$ (OH group hydrogen-bonded to CO). Under certain conditions the alcohol was obtained as a modification which had m. p. 182—183° (Found: C, 70·0; H, 4·7%); the two forms were interconvertible and gave identical infrared absorption curves.

Dehydrogenation of the Alcohol (XI; R = OH).—(*a*) The above hydroxy*iso*coumarin (0·82 g.) and 30% palladised charcoal [27] (0·24 g.) were heated at 220° under dry nitrogen for 1 hr. Water vapour was observed to be eliminated. The mixture was cooled and thoroughly extracted with boiling chloroform, and the solution filtered. Evaporation gave a yellowish-brown solid which was purified by chromatography on alumina in benzene solution. Chloroform-elution yielded 6′ : 7′-*methylenedioxynaphtho*(1′ : 2′-3 : 4)iso*coumarin* (XIII; $R^1 = R^2 =$ H, $R^3R^4 = O_2CH_2$) (40 mg.), which separated from dioxan in cream needles, m. p. 254—255° (Found: C, 73·9; H, 3·3. $C_{18}H_{10}O_4$ requires C, 74·5; H, 3·45%), $\lambda_{max.}$ 275 (ε 35,000), 307 (ε 12,400), and 335 mμ (ε 8500) (in $CHCl_3$), $\nu_{max.}$ 1272 and 1720 cm.$^{-1}$ (lactone-CO), 1502, 1573, 1600, 1613, and 1640 cm.$^{-1}$ (aromatic rings) (no OH band). The product was readily soluble in warm dilute alkali.

(*b*) A similar reaction with the hydroxy*iso*coumarin (0·26 g.) and 30% palladised charcoal (0·1 g.) at 270° for 30 min. gave, after purification by chromatography and elution with benzene, a compound which separated from dioxan in pale orange needles, m. p. 205° (40 mg.) (Found: C, 78·3; H, 3·9. $C_{18}H_{10}O_3$ requires C, 78·8; H, 3·7%), $\lambda_{max.}$ 255 (ε 38,000), 280 (ε 40,000), and 351 mμ (ε 7800) (in $CHCl_3$), $\nu_{max.}$ 1693, 1604, 1546, 1499, 1253, 954, 865, and 852 cm.$^{-1}$. This compound was insoluble in warm dilute alkali and gave a positive reaction towards Brady's reagent. It is considered to be 1′ : 2′-*methylenedioxy*-3 : 4-*benzofluorenone*. Subsequent chloroform-elution of the column gave a small yield of 6′ : 7′-methylenedioxynaphtho(1′ : 2′-3 : 4)*iso*coumarin, m. p. 254—255°, identical with that obtained as in (*a*).

Attempts to effect the dehydrogenation with palladised charcoal in boiling trichlorobenzene or with 5% rhodium–charcoal (Baker Platinum Co.) were unsuccessful.

[27] Linstead and Thomas, *J.*, 1940, 1130.

XUM

1′ : 2′-*Dihydro*-6′ : 7′-*methylenedioxynaphtho*(1′ : 2′-3 : 4)iso*coumarin* (XV).—The hydroxy-*iso*coumarin (XI; R = OH) (0·62 g.) in purified chloroform (100 c.c.) was cooled to 0° and a current of dry hydrogen chloride was passed into the solution for 30 min. After being washed with sodium hydrogen carbonate solution, the organic layer was dried (Na_2SO_4) and evaporated under reduced pressure. The residual *anhydro-compound* (XV) crystallised from benzene in needles, m. p. 188° (0·5 g.) (Found: C, 73·9; H, 4·2. $C_{18}H_{12}O_4$ requires C, 74·0; H, 4·1%), $\nu_{max.}$ 1690 cm.$^{-1}$ (lactone-CO) (no hydroxyl band), soluble in warm dilute alkali. The same product was obtained by the action of phosphorus halides on the alcohol. On one occasion the action of hydrogen chloride afforded 4′-*chloro*-1′ : 2′ : 3′ : 4′-*tetrahydro*-6′ : 7′-*methylenedioxynaphtho*(1′ : 2′-3 : 4)iso*coumarin* (XI; R = Cl), rhombic prisms [from light petroleum (b. p. 40—60°)], m. p. 125—126° (decomp.) (Found: C, 65·8; H, 3·7. $C_{18}H_{13}O_4Cl$ requires C, 65·8; H, 4·0%), having an infrared absorption for lactone-CO at 1715 cm.$^{-1}$ but no hydroxyl band.

Dehydrogenation of the compound (XV) (0·4 g.) by 30% palladised charcoal (0·1 g.) at 220° for 45 min. under nitrogen gave, as major product (25 mg.), the compound of m. p. 205° obtained by dehydrogenation of the hydroxy*iso*coumarin (XI; R = OH), together with a trace of compound (XIII; $R^1 = R^2 = H$, $R^3R^4 = O_2CH_2$).

Catalytic Hydrogenation of **1′ : 2′ : 3′ : 4′-*Tetrahydro*-6′ : 7′-*methylenedioxy*-4′-*oxonaphtho*-(1′ : 2′-3 : 4)iso*coumarin*** (IX).—The ketone (0·1 g.) in glacial acetic acid (15 c.c.) containing 60% perchloric acid (0·2 c.c.) was shaken in hydrogen with 5% palladised charcoal [28] for 5 hr.[16] (absorption 2 mol.). The filtered solution was poured into ice-water, and the product collected and crystallised from 50% acetic acid, from which it separated in needles, m. p. 163—164° (Found: C, 70·7; H, 4·8. $C_{18}H_{16}O_5$ requires C, 69·3; H, 5·1%), $\lambda_{max.}$ 232 (ε 16,900), 276 (ε 5530), 295 (ε 4480), and 318 mμ (ε 3900), $\nu_{max.}$ 3400 cm.$^{-1}$ (intense; CO_2H). The compound dissolved with effervescence in sodium hydrogen carbonate solution; it is formulated as 3-o-*carboxyphenyl*-1 : 2 : 3 : 4-*tetrahydro*-6 : 7-*methylenedioxy*-1-*naphthol* (XII).

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DEPARTMENT OF CHEMISTRY,
UNIVERSITY COLLEGE, CARDIFF. [*Received, February 26th*, 1958.]

[28] *Org. Synth.*, 1946, **26**, 78.

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532. *Studies in Polycyclic Systems. Part I. A New Synthesis of Picene.**

By D. NASIPURI.

Picene is prepared by a method starting with condensation of ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate with 2-1′-naphthylethyl bromide, the further rings being built on by Dieckmann condensation and reaction with the methiodide of 4-piperidinobutan-2-one. The method affords a convenient route also to methylpicenes and the preparation of 4-methyl- and 2 : 9-dimethyl-picene is reported.

A NUMBER of routes has been used for the synthesis of picene and its derivatives,[1] but most of them are lengthy and give a poor overall yield. In a more recent synthesis by Phillips,[2] the yield is comparatively high but the method involves separation of isomers in at least one stage. In view of the excellent results obtained by Wilds and his co-workers [3,4] in the preparation of chrysene derivatives by the application of the

* A preliminary account of this work appeared in *Chem. and Ind.*, 1956, 795, and in *Naturwiss.*, 1956, **43**, 469.

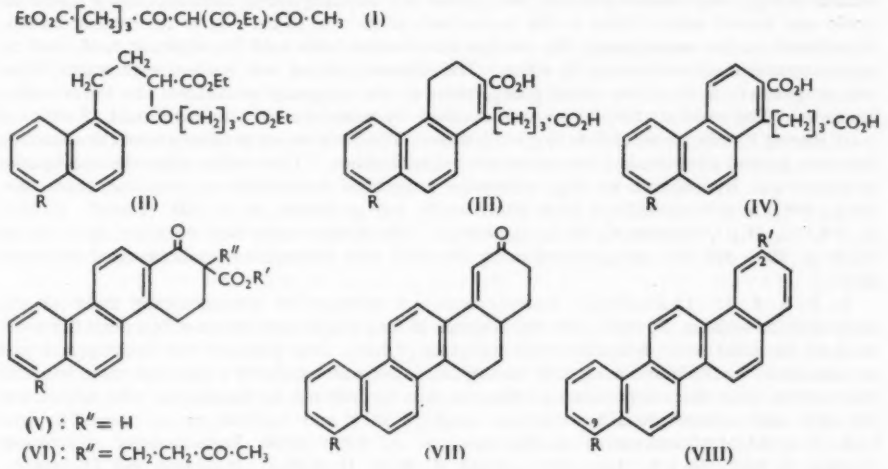
[1] Newman, *J. Org. Chem.*, 1944, **9**, 518, and references cited therein.

[2] (*a*) Phillips, *J. Amer. Chem. Soc.*, 1953, **75**, 3223; (*b*) Phillips and McWhorter, *ibid.*, 1955, **77**, 3856; (*c*) Phillips and Tuites, *ibid.*, 1956, **78**, 5438.

[3] Wilds and Shunk, *ibid.*, 1943, **65**, 469.

[4] Wilds and Werth, *J. Org. Chem.*, 1952, **17**, 1149.

Robinson–Mannich base synthesis [5] of unsaturated ketones, similar methods were investigated for the synthesis of alkylpicenes. Suitable starting materials would be 2-alkoxycarbonyl-1 : 2 : 3 : 4-tetrahydro-1-oxochrysenes (V). Ethyl 4 : 6-dioxoheptane-



1 : 5-dicarboxylate [6] (I) was therefore alkylated with 2-1′-naphthylethyl bromide; the product (II; R = H) on cyclodehydration with concentrated sulphuric acid and subsequent saponification gave γ-(2-carboxy-3 : 4-dihydro-1-phenanthryl)butyric acid (III; R = H) in an overall yield of 40%. The ester of the dihydro-acid was dehydrogenated with sulphur, and the dimethyl ester of the aromatic acid (IV; R = H) underwent Dieckmann cyclisation smoothly. The resultant sodio-derivative was treated *in situ* with a methanolic solution of 4-piperidinobutan-2-one methiodide [4] to afford the tetrahydrochrysene derivative (VI; R = H, R′ = Me) in about 60% yield. A preliminary attempt to cyclise this compound by two-stage aqueous alkaline procedure of Wilds and Close [7] proved unsatisfactory, presumably owing to the high melting point and low solubility. Cyclisation by acid, however, gave good results; the pentacyclic ketone (VII; R = H), obtained in about 70% yield, was reduced by lithium aluminium hydride, and the resultant alcohol was converted into picene by heating it with 30% palladium–charcoal.[8]

The Dieckmann condensation products of the dialkyl esters of the acids (III and IV; R = H) on hydrolysis gave 1 : 2 : 3 : 4 : 11 : 12-hexahydro- and 1 : 2 : 3 : 4-tetrahydro-1-oxochrysene respectively which were previously prepared by other workers.[9,10]

Lastly, the use of 2-(5-methyl-1-naphthyl)ethyl bromide [11] in the above series of reactions led to the substituted pentacyclic ketone (VII; R = Me) which was converted into (*a*) 4-methyl- and (*b*) 2 : 9-dimethyl-picene by (*a*) reduction with lithium aluminium hydride and (*b*) a Grignard reaction with methylmagnesium iodide, followed by dehydration and dehydrogenation with palladium–charcoal. The hydrocarbons were characterised by their ultraviolet absorption spectra and formation of 2 : 4 : 7-trinitrofluorenone complexes.[12]

[5] du Feu, McQuillin, and Robinson, *J.*, 1937, 53.
[6] Bardhan and Nasipuri, *J.*, 1956, 350.
[7] Wilds and Close, *J. Amer. Chem. Soc.*, 1946, **68**, 83.
[8] Linstead and Thomas, *J.*, 1940, 1127.
[9] Robinson and Thompson, *J.*, 1939, 1739.
[10] (*a*) Bachmann and Struve, *J. Org. Chem.*, 1940, **5**, 416; (*b*) Cook and Schoental, *J.*, 1945, 288.
[11] Bardhan, Nasipuri, and Mukherjee, *J.*, 1957, 921.
[12] Orchin and Woolfolk, *J. Amer. Chem. Soc.*, 1946, **68**, 1727.

Experimental

γ-(2-Carboxy-3 : 4-dihydro-1-phenanthryl)butyric Acid (III; R = H).—To a cold mixture of ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate (27·2 g.) and ethanolic sodium ethoxide [from sodium (2·3 g.) and ethanol (60 ml.)] was added 2-1′-naphthylethyl bromide (23·5 g.), and the whole was heated under reflux in the water-bath at 90° for 15 hr. After removal of most of the ethanol at the water-pump, the residue was treated with cold 2N-sulphuric acid, and the heavy organic matter taken up in ether. The ethereal extract was washed with water, dried, and evaporated, first at the water-pump, then at the oil-pump to remove the lower-boiling fractions. The residue (28—30 g.) was cyclised by concentrated sulphuric acid (2 vols.) at −10° during 15 min., in small lots (6 g.) at a time. The dark brown products from the combined lots were poured over crushed ice and extracted with ether. The residue after the evaporation of ether was hydrolysed by 5% ethanolic potassium hydroxide to give the crude *acid* (12 g., 40%) which crystallised from dilute acetic acid as prisms, m. p. 203° (Found: C, 73·7; H, 5·8. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·8%). The diethyl ester was obtained as a viscous oil, b. p. 220—225°/0·1 mm., by refluxing the acid with ethanol and concentrated sulphuric acid.

1 : 2 : 3 : 4 : 11 : 12-*Hexahydro-1-oxochrysene*.—A mixture of the foregoing ester (1 g.), finely divided sodium (70 mg.), and dry benzene (6 ml.) was heated under reflux until the formation of the solid sodio-derivative was complete (2 hr.). The product was decomposed with ice and dilute hydrochloric acid, and the organic layer was separated with some more benzene. The residue after the evaporation of benzene was hydrolysed by heating it with acetic acid (10 ml.) and concentrated hydrochloric acid (5 ml.) and worked up as usual, to give 1 : 2 : 3 : 4 : 11 : 12-hexahydro-1-oxochrysene, m. p. 159° (from benzene–light petroleum) (Found: C, 87·3; H, 6·7. Calc. for $C_{18}H_{16}O$: C, 87·1; H, 6·5%). Robinson and Thompson [9] give m. p. 154—156°.

γ-(2-Carboxy-1-phenanthryl)butyric Acid (IV; R = H).—The diethyl ester of the acid (III; R = H) (3·6 g.) was heated with powdered sulphur (0·32 g.) in a nitrate-bath at 245—250° for 2 hr. and the resultant brown product was taken up in ethanol and hydrolysed with potassium hydroxide in the usual way, to give the aromatic *acid* (3·2 g.) which crystallised from aqueous methanol in needles, m. p. 228° (Found: C, 74·1; H, 5·2. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). The *dimethyl ester* crystallised from methanol in needles, m. p. 72—73° (Found: C, 75·2; H, 6·1. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%).

1 : 2 : 3 : 4-*Tetrahydro-1-oxochrysene*.—The above dimethyl ester (1 g.) in a suspension of sodium (70 mg.) in dry benzene (7 ml.) was heated under reflux with the addition of one drop of methanol. Formation of sodio-derivative was completed in about 1 hr. The product was worked up and hydrolysed as described above, to give 1 : 2 : 3 : 4-tetrahydro-1-oxochrysene (0·40 g.) in light yellow plates (from benzene), m. p. 226—227° (Found: C, 87·6; H, 5·8. Calc. for $C_{18}H_{14}O$: C, 87·8; H, 5·7%). Bachmann *et al.*[10a] give m. p. 228—229° and Cook and Schoental [10b] 227—228°.

1 : 2 : 3 : 4-*Tetrahydro-2-methoxycarbonyl-1-oxo-2-3′-oxobutylchrysene* (VI; R = H, R′ = Me).—To the sodio-derivative of the oxo-ester (V; R = H, R′ = Me) prepared from the dimethyl ester of the acid (IV; R = H) (2·7 g.), sodium (200 mg.), and benzene (30 ml.) as described above, was added with cooling a solution of the methiodide of 4-piperidinobutan-2-one (2·5 g., 2 mol.) in anhydrous methanol (15 ml.). The solid disappeared after a few minutes' shaking and the solution was left at the room temperature overnight. Next day, the reaction was completed by refluxing the mixture in the steam-bath for 1 hr. After cooling, the solution was diluted with water, the precipitated solid was extracted thoroughly with hot benzene, and the benzene extract washed successively with water, dilute alkali, and dilute acid. After evaporation of the solvent, the residual solid crystallised from ethyl acetate, to give 1 : 2 : 3 : 4-*tetrahydro-2-methoxycarbonyl-1-oxo-2-3′-oxobutylchrysene* (1·9 g., 60%), m. p. 192—195°. Further crystallisations from ethyl acetate (charcoal) afforded plates, m. p. 209° (Found: C, 77·2; H, 5·9. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%). The corresponding *2-ethoxycarbonyl derivative* was also prepared from the diethyl ester of the acid (IV; R = H) in nearly the same yield and crystallised from ethyl acetate in cluster of plates, m. p. 195° (Found: C, 77·6; H, 6·3. $C_{25}H_{24}O_4$ requires C, 77·3; H, 6·2%).

2 : 3 : 4 : 4a : 5 : 6-*Hexahydro-2-oxopicene* (VII; R = H).—The above dioxo-ester (VI; R = H, R′ = Me) (2 g.) was refluxed in acetic acid (50 ml.), concentrated hydrochloric acid

(25 ml.), and water (5 ml.) for 15 hr. under nitrogen. After cooling, the mixture was diluted with water, and the precipitated solid was filtered off, to give the unsaturated *ketone* (VII; R = H) (1·1 g., 70%), m. p. 270—275°. Further crystallisations from benzene gave colourless crystals, m. p. 295° (Found: C, 88·7; H, 6·1. $C_{22}H_{16}O$ requires C, 88·6; H, 6·0%). The analogous 2-ethoxycarbonyl derivative (VI; R = H, R′ = Et) was similarly cyclised to the same ketone.

Picene.—A solution of the foregoing ketone (0·3 g.) in tetrahydrofuran (15 ml.) was added to lithium aluminium hydride (0·3 g.), suspended in ether (10 ml.), the mixture was heated under reflux for 1 hr., then decomposed with ethanol and dilute acid, and the organic matter was taken up into benzene and washed with water. The residue (0·3 g.) on evaporation of the solvent was heated with 30% palladium–charcoal (70 mg.) at 340° for 1 hr. The melt was extracted with hot benzene and, after evaporation, the product was sublimed in a high vacuum, to give picene (0·1 g.) which crystallised from xylene in fluorescent plates, m. p. 365—366° (Found: C, 94·8; H, 5·1. Calc. for $C_{22}H_{14}$: C, 95·0; H, 5·0%). The identity was confirmed by a mixed m. p. determination and ultraviolet absorption spectroscopy.[13] The 2 : 4 : 7-trinitrofluorenone derivative separated from benzene in red needles, m. p. 256—257° (Found: C, 70·5; H, 3·1; N, 7·3. Calc. for $C_{22}H_{14},C_{13}H_5O_7N_3$: C, 70·8; H, 3·2; N, 7·1%) (Orchin and Woolfolk [13] record m. p. 257—257·8°).

γ-(2-Carboxy-3 : 4-dihydro-8-methyl-1-phenanthryl)butyric Acid (III; R = Me).—2-(5-Methyl-1-naphthyl)ethyl bromide (25 g.) was added to a cold mixture of ethyl 4 : 6-dioxoheptane-1 : 5-dicarboxylate (27·2 g.) and ethanolic sodium ethoxide [from sodium (2·3 g.) and absolute ethanol (60 ml.)] and heated under reflux for 15 hr. The product was worked up in the usual way. The crude oxo-ester (II; R = Me) (38 g.), on cyclisation with sulphuric acid as described above, gave the *acid* (III; R = Me) (12 g.), m. p. 225° (from aqueous methanol) (Found: C, 73·8; H, 6·3. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%). The dimethyl ester boiled at 230—235°/0·1 mm.

γ-(2-Carboxy-8-methyl-1-phenanthryl)butyric Acid (IV; R = Me).—The preceding dihydro-ester was dehydrogenated with sulphur in the usual way and on hydrolysis afforded the *acid* (IV; R = Me) which crystallised from methanol in prisms, m. p. 238° (Found: C, 74·6; H, 5·7. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·5%). The *dimethyl ester* formed needles (from methanol), m. p. 113° (Found: C, 75·5; H, 6·3. $C_{22}H_{22}O_4$ requires C, 75·4; H, 6·3%).

1 : 2 : 3 : 4-Tetrahydro-2-methoxycarbonyl-7-methyl-1-oxo-2-3′-oxobutylchrysene (VI; R = R′ = Me).—The preceding ester (5 g.) was added to a suspension of sodium methoxide [from sodium (0·4 g.) and methanol (0·5 g.) in dry benzene (20 ml.)] and the mixture was refluxed for 2 hr. under nitrogen. To the sodio-derivative thus formed was gradually added, with cooling, a solution of the methiodide prepared from 4-piperidinobutan-2-one (5 g.) and the whole left overnight. The reaction was completed next day by 1 hour's heating on the steam-bath and the product was worked up as in the analogous case, to afford the *dioxo-ester* (VI; R = R′ = Me) (3·3 g., 65%), m. p. 233° (from ethyl acetate) (Found: C, 76·9; H, 6·3. $C_{25}H_{24}O_4$ requires C, 77·3; H, 6·2%).

2 : 3 : 4 : 4a : 5 : 6-Hexahydro-9-methyl-2-oxopicene (VII; R = Me).—The dioxo-ester (VI; R = R′ = Me) (1 g.) was heated with acetic acid (40 ml.), concentrated hydrochloric acid (20 ml.), and water (5 ml.) for 20 hr. under nitrogen. The solution was diluted with water, and the precipitate was collected and crystallised from benzene, to give the *ketone* (VII; R = Me) (0·5 g.), m. p. 313—314° (from benzene) (Found: C, 88·7; H, 6·3. $C_{23}H_{20}O$ requires C, 88·5; H, 6·4%).

4-Methylpicene (VIII; R = Me, R′ = H). The preceding ketone (200 mg.) was reduced by lithium aluminium hydride (100 mg.) in tetrahydrofuran (20 ml.), and the resultant alcohol was heated with 30% palladium–charcoal (40 mg.) at 340° for 1 hr., then sublimed in a high vacuum, to yield 4-methylpicene (80 mg.) which crystallised from chloroform in almost colourless leaflets, m. p. 370—372° (sealed tube) (Found: C, 94·3; H, 5·5. Calc. for $C_{23}H_{16}$: C, 94·5; H, 5·5%). Its 2 : 4 : 7-trinitrofluorenone complex formed a red powder (from acetic acid), m. p. 270° (Found: C, 71·05; H, 3·6; N, 7·0. Calc. for $C_{23}H_{16},C_{13}H_5O_7N_3$: C, 71·2; H, 3·5; N, 6·9%). Phillips and McWhorter [2b] give 372—374° and 267—268° as the respective m. p.s. The ultraviolet absorption spectrum is identical with that described by Phillips *et al.*

2 : 9-Dimethylpicene (VIII; R = R′ = Me).—A solution of the ketone (VII; R = Me) (300 mg.) in dry benzene (30 ml.) was treated with an excess of methylmagnesium iodide in

[13] Clar and Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 6235.

ether, and the resultant alcohol was dehydrated and dehydrogenated by 30% palladium–charcoal (80 mg.) at 340° for 1 hr. The product was taken up in hot benzene, chromatographed on alumina, and crystallised from benzene, to yield 2 : 9-dimethylpicene (140 mg.), m. p. 303—304° (Found: C, 93·8; H, 5·9. Calc. for $C_{24}H_{18}$: C, 94·1; H, 5·9%). It caused no m. p. depression when mixed with an authentic specimen and the ultraviolet absorption spectrum is very similar to that of picene. Ruzicka and Hofmann [14] give m. p. 305—306°, and Newman and Cline [15] 304·2—304·8°. The 2 : 4 : 7-trinitrofluorenone complex crystallised from benzene in red needles, m. p. 257° (Found: C, 71·4; H, 3·6; N, 6·9. Calc. for $C_{24}H_{18},C_{13}H_5O_7N_3$: C, 71·5; H, 3·7; N, 6·8%). Newman *et al.* give m. p. 257·8—258·6°.

The author thanks Professor J. C. Bardhan for his kind encouragement and Mrs. Chhabi Dutta for microanalyses. He is indebted to Professor M. S. Newman for gifts of picene and 2 : 9-dimethylpicene.

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[14] Ruzicka and Hofmann, *Helv. Chim. Acta*, 1937, **20**, 1155.
[15] Newman and Cline, *J. Org. Chem.*, 1951, **16**, 934.

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533. *Studies in Relation to Biosynthesis. Part XVI.* The Synthesis of Lumiflavin from Non-benzenoid Precursors.*

By A. J. BIRCH and C. J. MOYE.

Condensation of 5-amino-4-methylaminouracil (II; R = Me) with the aldol (I) from diacetyl produces the pteridine (III) (or the isomer with the pteridine section inverted) which can be cyclised by polyphosphoric acid to lumiflavin (IV; R = Me). These experiments are considered to represent a valid model reaction sequence for the biosynthesis of riboflavin.

IN Part XIII [1] the suggestion was made that the dimethylbenzene ring of riboflavin (IV; R = ribityl) arises biochemically from two molecules of diacetyl. This idea was supported by demonstrating that condensation of the aldol (I) derived from two molecules of diacetyl with 4 : 5-diaminouracil (II; R = H) gave a pteridine which was converted by alkali into lumichrome containing the dimethylbenzene ring. In order to provide a closer model we have now examined the condensation of the aldol (I) with 5-amino-4-methylaminouracil (II; R = Me) to give a pteridine (III) (or the isomer with the pteridine rings inverted). This pteridine could not be cyclised to the benzene derivative with alkali as in the previous work, possibly because of the greater sensitivity of lumiflavin to alkali. The action of polyphosphoric acid, however, readily produced lumiflavin (IV; R = Me) identified by comparison of ultraviolet and infrared spectra and by paper chromatography.

In the meantime further biochemical support for our hypothesis has been provided by Masuda [2] who identified acetoin in cultures of *Eremothecium ashbyii* and isolated compound (V; R = ribityl) from them. Goodwin and Treble [3] have also isolated 4 : 5-diaminouracil, as a derivative, from cultures of this organism. Masuda converted his compound (V; R = ribityl) into riboflavin by heating it with diacetyl. He prepared the analogue (V; R = Me) from the ribityl compound (V; R = ribityl) by illumination and synthesised it from the uracil derivative (II; R = Me) and diacetyl.[2] We have synthesised compound (II; R = Me) by a slightly different route and have converted it into compound (V; R = Me): the properties of the final product and of some intermediates are in reasonable, though not complete, agreement with those given by Masuda. We were unable to convert compound (V; R = Me) into lumiflavin by the action of diacetyl, possibly because

* Part XV, *J.*, 1958, 369.

[1] Birch and Moye, *J.*, 1957, 412.
[2] Masuda, *Pharm. Bull. (Japan)*, 1957, **5**, 28, 136.
[3] Goodwin and Treble, *Biochem. J.*, 1957, **67** 10P.

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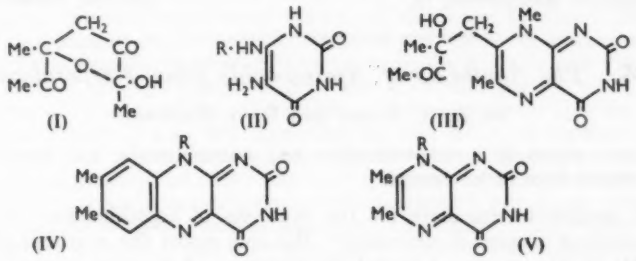
of the very sparing solubility of the pteridine. A small amount of the pteridine (III) was detected in the product by paper chromatography.

The natural occurrences and the results above, as well as the tracer results already cited,[1] strongly suggest the truth of our hypothesis as a *structural* one without distinguishing



the exact sequence of events. We believe that intervention of the semiketal (I) is more likely in a biochemical route than is the condensation of diacetyl with compound (V; R = ribityl), but only biochemical experiments can decide this.

Experimental

5-Amino-2 : 4-dihydroxy-6-methylaminopyrimidine (II; R = Me).—Our preparation of this compound was similar to that of Masuda [2] except that 2 : 4-dihydroxy-6-methylaminopyrimidine was made by King and King's method.[4] Reduction of 2 : 4-dihydroxy-6-methylamino-5-nitrosopyrimidine with sodium hydrogen sulphite [2] gave after crystallisation from water, not the bisulphite salt, m. p. 350° reported by Masuda,[2] but the free base, *5-amino-2 : 4-dihydroxy-6-methylaminopyrimidine*, m. p. 250—260° (Found: C, 36·3; H, 5·6; N, 33·75. $C_5H_8O_2N_4,0{\cdot}5H_2O$ requires C, 36·4; H, 5·45; N, 33·9%).

6 : 7 : 8-Trimethyl-lumazine.—The above pyrimidine (250 mg.) was heated in water (4 c.c.) to 80° for 10 min. with excess of diacetyl. The product (110 mg.) slowly crystallised at 0°, to give yellow needles, with a blue-green fluorescence in aqueous solution, m. p. 320—322° (Found: C, 52·3; H, 4·6. Calc. for $C_9H_{10}O_2N_4$: C, 52·4; H, 4·85%). Masuda [2] gives m. p. 300—301°. After being refluxed with diacetyl (5 c.c.) for 10 hr. the substance was recovered almost entirely.

Lumiflavin.—The above aminodihydroxymethylaminopyromidine (400 mg.) in water (5 c.c.) was shaken with 5-acetyltetrahydro-2-hydroxy-2 : 5-dimethyl-3-oxofuran [1] (300 mg.) for 2 min. The golden-yellow solution was left at 0° for several days; golden cubes, m. p. 346—348° (240 mg.), separated which could not be recrystallised and were analysed after being washed and dried. They were either *7-(2-hydroxy-2-methyl-3-oxobutyl)-6 : 8-* or *6-(2-hydroxy-2-methyl-3-oxobutyl)-7 : 8-dimethyl-lumazine* (Found: C, 52·6; H, 5·35. $C_{13}H_{16}O_4N_4$ requires C, 53·4; H, 5·5%), and had $\lambda_{max.}$ (in H_2O) 257, 277, 405 mμ (ε 14,230, 10,150, 11,150), $\lambda_{min.}$ 225, 272, 336 mμ (ε 7425, 9800, 330), $\lambda_{inflex.}$ 302 mμ (ε 1245).

Attempted recrystallisation from hot water led to dark green crystals with a different absorption spectrum (in H_2O) [$\lambda_{max.}$ 235, 300, 445 mμ (ε 14,750, 12,649, 17,762), $\lambda_{min.}$ 270, 352 mμ (ε 4890, 680), $\lambda_{inflex.}$ 253 mμ (ε 10,450)] but a similar analysis (Found: C, 54·0; H, 5·3%). This may be the substance produced by dehydration of the aldol part of the molecule which then crystallises with a mole of water.

The pteridine, m. p. 346—348° (20 mg.), was added to polyphosphoric acid (4 c.c.) at 90°. Heating was continued for 30 min., water (50 c.c.) added, and the solution saturated with sodium acetate and extracted with chloroform. After evaporation the product was purified by chromatography on paper strips in butanol–ethanol–water (50 : 15 : 35) and had R_F 0·35. The product was eluted from the paper with methanol, the solvent evaporated, and the lumiflavin separated from some paper extractives by dissolution in water. Saturation of the aqueous solution with sodium acetate and extraction with chloroform gave lumiflavin, identical

[4] F. E. and T. J. King, *J.*, 1947, 726; Winkelman, *J. prakt. Chem.*, 1927, **115**, 202.

in ultraviolet spectrum ($\lambda_{max.}$ 225, 269, 372, 445 mμ; $\lambda_{min.}$ 242, 300, 400 mμ) and infrared spectrum with a specimen kindly provided by Dr. T. W. Goodwin (Liverpool). The R_F (0·35) on paper in the above system was identical with that of an authentic specimen and the fluorescence colour was the same.

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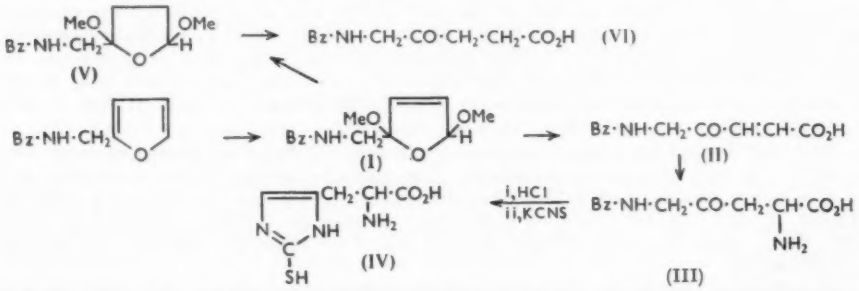
534. *The Synthesis of Amino-acids from Furfurylamine.*

By A. A. MAREI and R. A. RAPHAEL.

New routes to mercaptohistidine and δ-aminolævulic acid have been developed from furfurylamine.

AN obvious possible intermediate for the synthesis of ergothioneine [1] is the hitherto unknown 5-amino-4-oxopent-2-enoic acid.[2] We now report the synthesis of the benzoyl derivative (II) of this compound from furfurylamine and describe its reactions.

Benzoylation of furfurylamine and electrolytic methoxylation [3] of the resulting derivative furnished the two diastereoisomers of the dihydrodimethoxyfuran (I). Treatment of these with chromium trioxide in dilute sulphuric acid resulted in fission of the hemiacetal linkages, followed by oxidation of the keto-aldehyde produced to furnish directly the crystalline 5-benzamido-4-oxopent-2-enoic acid (II). Many attempts at a preliminary hydrolysis with acid alone, in order to isolate the intermediary keto-aldehyde,



were unsuccessful. Addition of ammonia to the double bond of this compound gave the α-amino-acid (III); the position of the amino-group in this product could be confidently predicted from earlier analogous additions.[4] This orientation was confirmed by benzoylation to 2 : 5-dibenzamido-4-oxopentanoic acid and conversion of this into its methyl ester, a known degradation product of histidine.[5,6] Hydrolysis of the amino-acid (III) to 2 : 5-diamino-4-oxopentanoic acid dihydrochloride and treatment of the latter with potassium thiocyanate [6] furnished mercaptohistidine (IV).

In a synthetic approach to ergothioneine attempts were made to effect the addition of dimethylamine to the unsaturated acid (II), by using the techniques which had proved successful with ammonia. Surprisingly no pure product could be obtained. An attempt to obtain the required compound by reductive alkylation of the amino-acid (III) with formaldehyde proved equally fruitless.

Catalytic hydrogenation of the dihydrofuran (I) yielded the tetrahydrofuran (V) which, on hydrolysis and oxidation with chromium trioxide–sulphuric acid, was smoothly

[1] For a review see Bell, *Ann. Reports*, 1955, **52**, 285.
[2] For a previous attempted synthesis see Wynn and Corwin, *J. Org. Chem.*, 1950, **15**, 203.
[3] Clauson-Kaas and Tyle, *Acta Chem. Scand.*, 1952, **6**, 667.
[4] Fraser and Raphael, *J.*, 1950, 2245.
[5] Windaus, Dörries, and Jensen, *Ber.*, 1921, **54**, 2745.
[6] Heath, Lawson, and Rimington, *J.*, 1951, 2215.

converted into δ-benzamidolævulic acid; acid hydrolysis furnished the parent amino-acid hydrochloride.

Experimental

N-Benzoylfurfurylamine.—Benzoyl chloride (80 g.) was added dropwise to a cooled stirred solution of freshly distilled furfurylamine (48·5 g.) in 2N-sodium hydroxide (400 ml.). After a further hour's stirring at room temperature the solid was filtered off, washed with water, and crystallised from methanol or benzene, to give the *amide* (96 g.), m. p. 104° (Found: C, 71·8; H, 5·45; N, 6·75. $C_{12}H_{11}O_2N$ requires C, 71·6; H, 5·5; N, 6·95%).

cis- *and* trans-2-*Benzamidomethyl*-2 : 5-*dihydro*-2 : 5-*dimethoxyfuran* (I).—(*a*) A solution of *N*-benzoylfurfurylamine (30·2 g.) and ammonium bromide (2·6 g.) in methanol (260 ml.) was electrolysed in the cell already described [7] for 7 hr. at −12°. The current dropped from 4·0 to 0·6 amp. and the potential difference rose from 14·0 to 16·2 v during the reaction. The cell contents were then poured into sodium methoxide solution (0·7 g. of sodium in 10 ml. of methanol), and the methanol removed under reduced pressure. The residue was triturated with warm dry ether (250 ml.) and the filtered solution allowed to evaporate slowly to small bulk. The resulting solid was filtered off and crystallised from concentrated ethereal solution, to furnish one *diastereoisomer* (I) (10·8 g.), m. p. 109—110° (Found: C, 64·2; H, 6·45; N, 5·35. $C_{14}H_{17}O_4N$ requires C, 63·85; H, 6·5; N, 5·3%). Evaporation of the ether solutions gave the other *isomer* (I) (18·9 g.) as a very viscous oil, b. p. 140°/10^{-4} mm. (Found: C, 63·8; H, 6·4; N, 5·6%).

(*b*) To a stirred solution of *N*-benzoylfurfurylamine (10 g.) in dry methanol (75 ml.) and ether (40 ml.) at −25° was added dropwise a cold solution of bromine (2·8 ml.) in methanol (15 ml.) at such a rate that the temperature never rose above −20°. The mixture was stirred for 1 hr. at −20°, then cooled to −40° and treated with gaseous ammonia, the temperature being kept below −5°. The mixture was allowed to attain room temperature and stirred for a further 30 min.; dry ether (300 ml.) was then added and the precipitated ammonium bromide filtered off. The evaporated filtrate was treated as in (*a*), to yield the solid (3·6 g.) and the liquid (4·1 g.) diastereoisomer (I). The presence of potassium acetate during the addition of the bromine did not materially affect the yield.

5-Benzamido-4-oxopent-2-enoic Acid (II).—To a stirred solution of the mixed isomers (I) (5·2 g.) in acetone (60 ml.) at 0° was added a cold solution of chromium trioxide (10 g.) in water (30 ml.) and concentrated sulphuric acid (8·5 ml.) at such a rate that the temperature did not exceed 20°. Stirring was continued at 20° for 1 hr. and the chromium salts were then precipated by addition of acetone (250 ml.). The filtered solid was washed with dry acetone, and the combined filtrates were evaporated under reduced pressure at 20°. Crystallisation of the residue was induced by scratching and completed at 0° in 15 hr. The solid was filtered off, washed with a little ice water, dried, and recrystallised from ethyl acetate, to yield the *keto-acid* (II) (1·2 g.), m. p. 140—142° (decomp.) (Found: C, 61·9; H, 4·75; N, 6·05. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·75; N, 6·0%), $\lambda_{max.}$ 225 and 350 mμ (ε 11,900 and 5400 in EtOH), $\nu_{max.}$ (KBr disc) 690, 950, 1555, 1650, and 1750 cm.$^{-1}$. Attempted aerial oxidation of the furan (I) in the presence of cobalt acetate [8] proved fruitless, as did the action of bromine followed by silver oxide [9] on *N*-benzoylfurfurylamine.

2-Amino-5-benzamido-4-oxopentanoic Acid (III).—The keto-acid (II) (5 g.) was dissolved in ammonia (30 ml.; *d* 0·88) and kept at room temperature for 16 hr. The mixture was taken to dryness under reduced pressure and the residual solid triturated with ethanol. Filtration and crystallisation from ethanol–water gave the *amino-acid* (III) (1·8 g.), m. p. 178—179° (decomp.) (Found: C, 57·4; H, 5·85; N, 11·05. $C_{12}H_{14}O_4N_2$ requires C, 57·6; H, 5·65; N, 11·2%). Use of liquid ammonia produced a comparable yield. Hydrolysis with hydrochloric acid and conversion of the resulting dihydrochloride into mercaptohistidine followed exactly previous proceedings.[6] Schotten–Baumann benzoylation of the amino-acid yielded 2 : 5-*dibenzamido*-4-*oxopentanoic acid*, m. p. 214° (from methanol) (Found: C, 64·2; H, 5·3; N, 7·6. $C_{19}H_{18}O_5N_2$ requires C, 64·4; H, 5·1; N, 7·9%). Esterification of this acid with methanolic hydrogen chloride or diazomethane furnished the known methyl ester, m. p. 173° (lit., m. p. 173° [5] and 158° [6]) (Found: C, 65·5; H, 5·5; N, 7·6. Calc. for $C_{20}H_{20}O_5N_2$: C, 65·2; H, 5·5; N, 7·6%).

[7] Clauson-Kaas, Limborg, and Glens, *Acta Chem. Scand.*, 1952, **6**, 531.
[8] McKeever, U.S.P. 2,583,112; *Chem. Abs.*, 1952, **46**, 8670.
[9] Carter, *J. Amer. Chem. Soc.*, 1928, **50**, 2299.

2-Benzamidomethyltetrahydro-2 : 5-dimethoxyfuran (V).—A solution of the solid isomer of the dihydrofuran (I) (4·3 g.) in methanol (50 ml.) was hydrogenated in the presence of 10% palladium–charcoal (0·5 g.). Filtration, removal of solvent, and distillation gave the *tetrahydrofuran* (V) (4·1 g.), b. p. 146°/0·1 mm. (Found: C, 63·4; H, 7·15; N, 5·3. $C_{14}H_{19}O_4N$ requires C, 63·4; H, 7·2; N, 5·3%).

δ-Aminolævulic Acid.—To a stirred solution of the above tetrahydrofuran (2 g.) in acetone (10 ml.) at 0° was added a solution of chromium trioxide (3·5 g.) in water (10 ml.) and concentrated sulphuric acid (2·8 ml.) at such a rate that the temperature did not rise above 20°. After a further 30 minutes' stirring at room temperature water (30 ml.) was added, the acetone removed under reduced pressure, and the residue extracted first with ether, then with ethyl acetate. The combined extracts were dried ($MgSO_4$) and evaporated; the resulting solid crystallised from ethyl acetate, to give *δ-benzamidolævulic acid* (VI) (1·7 g.) as prisms, m. p. 118—119° (Found: C, 61·35; H, 5·6; N, 5·9. $C_{12}H_{13}O_4N$ requires C, 61·3; H, 5·6; N, 5·95%). The same compound was obtained by catalytic hydrogenation of the unsaturated keto-acid (II). Esterification with ethanolic hydrogen chloride furnished the known ethyl ester, prisms, m. p. 101° (from aqueous ethanol) (lit.,[5] m. p. 101°). Heating the acid for 4 hr. with concentrated hydrochloric acid gave a quantitative yield of the hydrochloride of δ-aminolævulic acid which crystallised from methanol–ether in needles, m. p. 144—147° (decomp.) as recorded.[2]

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535. *Physicochemical Studies on Starches. Part XIII.* The Fractionation of Oat and Wheat Starches.*

By A. W. ARBUCKLE and C. T. GREENWOOD.

The behaviour of laboratory-prepared oat and wheat starches on fractionation by dispersion and aqueous leaching has been critically examined. Aqueous leaching at various temperatures resulted in sub-fractionation of the amylose. The physical properties of the various starch-products have been determined and are discussed.

SATISFACTORY fractionation of laboratory-prepared cereal starches into their component amylose and amylopectin appears to be more difficult [1,2] than is the case for potato starch. This paper deals with the problems for oat and wheat. The effect of variations in methods of fractionation on molecular size and β-amylolysis limits of the amylose has been examined. Results are discussed with regard to the structure of amylose and the nature of the granule.

EXPERIMENTAL METHODS

Preparation of the Starches.—Starch was isolated from oats (var. Milford) and wheat (var. Victor II) by aqueous extraction of the defatted grain, and was purified from protein by Anderson and Greenwood's method.[3] The starches were then exhaustively defatted with boiling 80% methanol. A commercial sample of wheat starch was also studied.

Leaching and Dispersing Procedures.—The methods employed to fractionate the starches in a nitrogen atmosphere by (i) aqueous leaching at 70° and 98°, and (ii) complete dispersion of the granular structure with and without pretreatment with M-potassium hydroxide at 0° were as described elsewhere,[4] with the exception that some dispersions were carried out in the presence of phosphate buffer (pH 6·5; 2 ml./100 ml. of dispersion).

* Part XII, *J.*, 1958, 711.

[1] MacWilliam and Percival, *J.*, 1951, 2259.
[2] Greenwood and Das Gupta, *J.*, 1958, 707.
[3] Anderson and Greenwood, *J. Sci. Food Agric.*, 1955, **6**, 587.
[4] Cowie and Greenwood, *J.*, 1957, 2862, 4640.

Characterization of Starch Products.—Measurements were made of (i) iodine affinity, (ii) limiting viscosity number $[\eta]$ in M-potassium hydroxide, and (iii) β-amylolysis conversion limit. (See earlier papers in this Series.)

Properties of Whole Starches.—The properties of the whole starches were:

Starch	Protein (%) [a]	I.A.[b]	Amylose (%) [c]	$\overline{R}$ [d]	C.L. for amylopectin
Oat	0·24	5·13	27·0	26·8	19·6
Wheat	0·33	5·00	26·3	25·6	18·9

[a] % N × 6·25. [b] Iodine affinity. For both starches (I.A./19·0) × 100. [d] Ratio of terminal to non-terminal groups from HIO_4 oxidation (see ref. 5). [e] Conversion limit, calc. from previous column.

Results and Discussion

For both starches, the purely physical methods of purification used did not reduce contaminating protein to below about 0·3%, a value about ten times greater than that for potato starch. Johnston's method [6] involving extraction with 1% ammonium oxalate was also not satisfactory. Tightly bound protein appears to be, in fact, a characteristic of these laboratory-prepared granular starches. Its significance with regard to granular structure is not known, but it might well hinder the swelling properties and so influence its dispersive properties. The salient features of the results of various fractionation

Table 1. *Properties of the components from oat starch.*

		Amylopectin		Amylose				
							Conversion limit [e]	
Expt.	Method of fractionation	Purity (%) [a]	% of total amylose retained [b]	I.A.[c]	$[\eta]$ in M-KOH	D.P.[d]	(i)	(ii)
F1	70° Aqueous leach	82	67	19·1	160	1190	95	100
F2	98° Aqueous leach	94	23	18·0	340	2500	79	97
F3	Thymol–Bu^{n}OH dispersion without buffer	92	31	13·7	180	1330	71	86
F4	Thymol–Bu^{n}OH dispersion with buffer (pH 6·47)	93	27	14·7	212	1570	—	—
F5	KOH-pretreatment	99	<4	16·8	263	1950	72	91

[a] Calc. from (iodine affinity/19·0) × 100. [b] % of total amylose in starch retained as impurity in the amylopectin. Calc. by assuming original starch to contain 27% of amylose. [c] Iodine affinity. [d] Approx. degree of polymerization. Calc. from $\overline{D.P.} = 7{\cdot}4\,[\eta]$ (see text). [e] β-Amylolysis limits for (i) pure β-amylase, and (ii) β-amylase + Z-enzyme. Expressed as % conversion into maltose. Accuracy ± 2%.

Table 2. *Properties of the components from wheat starch.*

		Amylopectin		Amylose				
							Conversion limit [e]	
Expt.	Method of fractionation	Purity (%) [a]	% of total amylose retained [b]	I.A.[c]	$[\eta]$ in M-KOH	D.P.[d]	(i)	(ii)
F6	70° aqueous leach	81	74	17·8	145	1070	98	—
F7	98° aqueous leach	94	23	15·8	300	2240	66	89
F8	Thymol–Bu^{n}OH dispersion without buffer	96	12	19·0	260	1920	65	96
F9 [f]	Thymol–Bu^{n}OH dispersion without buffer	95	18	17·2	133	980	—	—
F10	Thymol–Bu^{n}OH dispersion with buffer (pH 6·47)	96	12	17·6	280	2060	—	—
F11	KOH-pretreatment	96	12	18·0	258	1910	—	—

[a] Calc. from (iodine affinity/19·0) × 100. [b] Calc. as for Table 1 by assuming original starch to contain 26·3% of amylose. [c] As for Table 1. [f] Commercial starch.

experiments are summarized in Tables 1 and 2. Values for the average degree of polymerization of the amylose ($\overline{D.P.}$) were calculated by using the relation previously obtained for potato amylose.[4] Although this may not be extremely accurate, the calculated values are likely to be of the correct order of magnitude.

[5] Anderson and Greenwood, *J.*, 1955, 3016.
[6] Johnston, *Nature*, 1956, **178**, 370.

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Whilst sub-fractionation of the amylose component by aqueous leaching of the granules at various temperatures was satisfactory, both starches proved extremely difficult to disperse before conventional fractionation by precipitants. Resulting dispersions were turbid even after two hours' boiling, and addition of either sodium chloride or phosphate buffer (pH 6·47) made no improvement. Preliminary experiments with oat starch made in collaboration with Mr. J. M. G. Cowie had shown thymol to be a more suitable initial precipitant than *cyclo*hexanol, butan-1-ol, pentanol, or pyridine. This reagent was used therefore for wheat. Difficulty was found in recrystallizing both amyloses from butan-1-ol solutions; in some instances, an iodine affinity of 19·0% (the maximum value found for these amyloses: cf. ref. 5) could not be achieved.

The limiting viscosity numbers of the 98°-leached products (F2 and F7) were higher than for the other amylose fractions. This suggests that degradation must have occurred during the dispersion—even in a nitrogen atmosphere—and the two amyloses appear to be more susceptible to hydrolysis than potato amylose. (For example, when amylose F2 was heated in boiling water in the presence of nitrogen for 1 hr., $[\eta]$ decreased from 340 to 260, whilst for amylose F7 under similar conditions $[\eta]$ decreased from 300 to 280.)

Fractionation Conditions.—In view of the apparent lability of the amylose components of oat and wheat starch, fractionation by aqueous leaching at 98° (cf. ref. 7) yields amylose of higher purity and limiting viscosity number than does a conventional dispersion. However, the purity of the amylopectin obtained by this method may not be high (cf. also refs. 4 and 8). For laboratory-prepared cereal starches, as has already been found for *Zea mays* starch,[2] the method [9] involving pretreatment with M-potassium hydroxide at 0° appears to be most satisfactory; it yields purer amylopectin, and amylose which is relatively little degraded.

Fractionation of Commercial Wheat Starch.—The sample of commercial wheat starch gave an amylose with a low limiting viscosity number. The decrease was relatively much larger than between laboratory- and commercially-prepared potato starch.[4] This is related perhaps to the more vigorous purification necessary to remove protein in the manufacture of cereal starches.

Uniformity of Structure of Amylose.—To investigate whether the different amylose fractions were linear or contained some branch-point or other anomaly, β-amylolysis experiments were carried out (see Tables 1 and 2). The concurrent action of β-amylase and Z-enzyme [10] enabled another calculation to be made of the amount of amylopectin impurity in some fractions; this value agreed well with that from iodine affinity measurements. Table 3 summarises the results and previous values obtained for potato amylose.[4]

TABLE 3. *Comparison of β-amylolysis limits for various fractions of amylose from laboratory-prepared starches.*

	Potato †			Oat			Wheat		
Prep. of sample in N_2	% of total amylose	$[\eta]$	β-limit *	% of total amylose	$[\eta]$	β-limit *	% of total amylose	$[\eta]$	β-limit *
Aq. leaching at 70°	40	240	100	33	160	95	28	145	98
Aq. leaching at 98°	80	370	86	77	340	80	77	300	69
Dispersion of granule ...	100	440	77	100	180	77	100	260	66

† Results from ref. 4. * Expressed as % conversion into maltose. Calculated by assuming 56% conversion of any amylopectin impurity into maltose.

The same general trend for the β-amylolysis limits of the different fractions is observed as for potato starch.[4] Leaching at 70° caused limited swelling of the granules and enabled short-chain, essentially linear amylose (as shown by its high conversion into maltose) to

[7] Baum, Gilbert, and Wood, *J.*, 1955, 4047.
[8] Bengough, Stanwix, and Steedman, *Chem. and Ind.*, 1957, 1241.
[9] Potter, Silveira, and McCready, *J. Amer. Chem. Soc.*, 1953, **75**, 1335.
[10] See Cowie, Fleming, Greenwood, and Manners, *J.*, 1958, 697.

diffuse out. Extraction at higher temperatures gave amylose which was incompletely hydrolysed, the amount of resistant material increasing with increase in temperature and consequent swelling and disruption of the granule. The difficulties in determining the nature of the barrier to β-amylolysis have been discussed elsewhere,[11] but it is thought that since disruption of the granule is involved, branching in the amylose is not improbable.[4]

For oat amylose, if about 35% is linear, and the whole is hydrolysed to 77% with β-amylase, then the portion containing an anomaly must be hydrolysed to about 65%. For wheat amylose, similar calculations show that the portion containing an anomaly must be hydrolysed to about 50%. These results suggest that the barrier to β-amylolysis in these amyloses is again essentially randomly situated (cf. ref. 10).

Although Peat,[12] Hopkins,[13] and Hassid,[14] with their collaborators, have suggested that pure β-amylase converts only about 70% of amylose into maltose, our experiments on amylose sub-fractions indicate that amyloses obtained by dispersive methods consist of two types of molecule, some being linear and others having a randomly situated barrier to this enzymic hydrolysis. On this basis, the percentage of linear material (L) in any amylose fraction can be calculated to the first approximation from the expression: $(T - L)/(100 - L) = 1/2$, where T = the percentage conversion into maltose for the total fraction. Values of L from calculation and experimental determination may not agree, since the aqueous leaching is not necessarily quantitative. The results from such calculations (*i.e.*, potato, *ca.* 55; oat, *ca.* 55; wheat, *ca.* 30%) suggest that the amount of linear material may vary from starch to starch.

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[11] Cowie, Fleming, Greenwood, and Manners, *J.*, 1957, 4430.
[12] Peat, Pirt, and Whelan, *J.*, 1952, 705, 714.
[13] Hopkins and Bird, *Nature*, 1953, **172**, 492.
[14] Neufeld and Hassid, *Arch. Biochem. Biophys.*, 1955, **59**, 405.

NOTES.

536. *Physicochemical Studies on Starches. Part XIV.*[1] *The Effect of Acid on Wheat-starch Granules.*

By A. W. ARBUCKLE and C. T. GREENWOOD.

THE effect of acid on potato-starch granules has been described in Part V.[2] During further studies of granular structure, its effect on wheat-starch granules has been investigated.

Experimental.—Wheat starch (var. Victor II) was isolated and purified as in Part XIII.[1] Methods used to treat the granules with acid in a nitrogen atmosphere, to measure the overall effect of acid-treatment on the granules, and to characterize the fractionation products were as for the previous investigation on potato starch.[2]

Initial experiments were carried out by treating the granules with 0·2M-hydrochloric acid at 45°. Potentiometric iodine titration on the products showed changes analogous to those observed for potato granules: there was an apparent increase in iodine-uptake for the first 2 hr., and a decrease thereafter. In addition, the slope of the linear portion of the curve increased with time of acid-treatment, as did the activity of free iodine necessary to

[1] Part XIII, Arbuckle and Greenwood, preceding paper.
[2] Cowie and Greenwood, *J.*, 1957, 2658.

saturate the amylose. These results and those obtained on treating the granules with M-hydrochloric acid at 16° were as shown.

Time of acid-treatment (hr.)		0	1	2	4	6	8	24
For 0·2M-HCl at 45°	Iodine affinity	5·0	5·2	5·5	4·4	3·8	—	1·5
	Amylose (%) †	26·3	27·3	29·0	23·7	20·0	—	7·9
For M-HCl at 16°	Iodine affinity	5·0	—	5·3	5·7	—	5·6	4·8
	Amylose (%) †	26·3	—	28·0	30·0	—	29·5	25·3

† Apparent % of amylose calc. by assuming iodine affinity of amylose = 19·0 (see ref. 5).

The properties of the fractionated components from the acid-treated starches were as shown in Table 1. Degrees of polymerization ($\overline{D.P.}$) were calculated on the assumption that the relation found for potato amylose [3] holds in order to show the order of magnitude of the changes involved. Fractionation of the acid-treated starches proved more difficult than for the original starch. A similar effect was found by Kerr [4] for maize starch.

TABLE 1. *Properties of the fractionated components.*

0·2M-HCl at 45°

Acid-treatment (hr.)	Amylose I.A.[a]	Amylose $[\eta]$ [b]	Amylose $\overline{D.P.}$ [c]	Amylopectin I.A.[a]	Amylopectin % Amylose [d]	Amylopectin $[\eta]$ [b]	Amylopectin $10^{13} S_{20}$ [e]
0	19·0	260	1920	0·5	3	140	121
1	10·3	178	1320	—	—	80	28
2	11·2	164	1210	—	—	60	22
4	12·5	140	1030	0·5	3	—	—
6	14·8	134	990	0·8	4	50	19
24	—	—	—	—	—	30	5

M-HCl at 16°

Acid-treatment (hr.)	Amylose I.A.[a]	Amylose $[\eta]$ [b]	Amylose $\overline{D.P.}$ [c]	Amylopectin I.A.[a]	Amylopectin % Amylose [d]	Amylopectin $[\eta]$ [b]	Amylopectin $10^{13} S_{20}$ [e]
0	19·0	260	1920	0·5	3	140	121
2	12·6	235	1740	0·7	4	175	110
4	16·8	212	1570	1·5	8	110	80
8	18·7	188	1390	1·1	6	140	85
24	—	150	1110	0·8	4	160	56

[a] Iodine affinity (see ref. 5). [b] Measured in M-KOH. [c] Calc. from $\overline{D.P.} = 7{\cdot}4[\eta]$ (see ref. 3). [d] % of amylose impurity calc as in ref. 3. [e] Sedimentation constant in c.g.s. units at $c = 0{\cdot}2$ g./100 ml.

Discussion.—Potentiometric iodine titrations suggested that amylopectin was preferentially solubilized to give an increase in the apparent amount of linear material in the granule. The amount of reducing sugar in the acid supernatant liquid was, however, small as shown by chromatography.

The rate of degradation of the *amyloses* was expressed as (1) the number of bonds broken per initial molecule, and (2) $1/[\eta]$, both as a function of time.[2,6] For the products isolated after treatment with 0·2M-acid at 45°, the graphs of these functions were essentially similar to those for potato, and the extrapolated curves did not pass through the origin (cf. Fig. 3 of ref. 2). The linear portion corresponded, however, to a rate of only 0·1 bond broken per initial molecule per hour, which is 4—5 times slower than that for potato. For the M-acid at 16°, degradation was limited (*ca.* 0·05), and there was no evidence of any initial preferential breakdown.

Degradation of the *amylopectins* was calculated from the plot of $1/S$ *versus* t. For the reasons already given,[2] this must be a minimum rate. The samples isolated after treatment with 0·2M-acid at 45° showed an initial preferential breakdown, which was much larger than that for amylose and may well represent attack on amylopectin in the outer surface or amorphous regions (cf. ref. 2). The linear portion of the curve corresponded to a rate of about 0·4 (same units as above), which was slower than that for potato amylopectin. At

[3] Cowie and Greenwood, *J.*, 1957, 2862.
[4] Kerr, *Stärke*, 1952, **4**, 39.
[5] Anderson and Greenwood, *J.*, 1955, **3016**.
[6] Bryce and Greenwood, *J. Polymer Sci.*, 1957, **25**, 480.

16°, the M-acid caused relatively little degradation (*i.e.*, a rate of *ca.* 0·07), although more than for the corresponding amylose, and in contrast to the results at 45° there was only limited initial preferential breakdown.

The effect of treating wheat-starch granules with 0·2M-acid at 45° could be explained by attack by acid in the manner already suggested for potato starch.[2] The calculated rates of degradation of the two components are, however, less than for potato. This may be related to a more compact structure for wheat starch, and thus an increased resistance to dispersion and fractionation.[1] The very limited accessibility of the granules is emphasized by the relatively negligible effect of M-hydrochloric acid at 16° on the molecular size of the components.

These studies suggest that there may be some fundamental difference in granular structure between tuber and cereal starches. Further methods of examining this are therefore being investigated.

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537. *Quaternary Ammonium Salts. Part V.* The Effect of Different Nucleophilic Reagents on the Mode of Decomposition of Quaternary Ammonium Salts.*

By WADIE TADROS, ALFY BADIE SAKLA, and MOHEB SADEK ISHAK.

THIS paper reports that the mode of decomposition of quaternary ammonium salts possessing an activating *para*-substituent in a benzene nucleus may be affected by the nature of the nucleophilic reagent used (see Table).

Salt	Reagent	Solvent	Products [a]
$CO(C_6H_4\cdot NMe_3I\text{-}p)_2$	OEt^- [b]	95% EtOH [b]	$CO(C_6H_4\cdot OEt)_2$ (50—55%); $EtO\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot NMe_3$ (20—25%); Michler's ketone (5—10%); $EtO\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot OH$ (trace)
	CN^- [d]	,,	Michler's ketone; $EtO\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot NMe_2$ (trace)
	$HO\cdot C_6H_4\cdot O^-$	$(CH_2\cdot OH)_2$	$CO(o\text{-}C_6H_4\cdot C_6H_4\cdot OH)_2$ [e] & Michler's ketone (mainly)
$p\text{-}NC\cdot C_6H_4\cdot NMe_3Cl$	OEt^- [f]	95% EtOH [b]	$p\text{-}NMe_2\cdot C_6H_4\cdot CO\cdot NH_2$ (40—45%); $p\text{-}OEt\cdot C_6H_4\cdot CO\cdot NH_2$ (35—40%); $p\text{-}NMe_2\cdot C_6H_4\cdot CO_2H$ (a little)
$p\text{-}NO_2\cdot C_6H_4\cdot NMe_3Cl$	OEt^- [g]	EtOH	$p\text{-}NO_2\cdot C_6H_4\cdot OEt$ [g]
	OMe^- [h]	MeOH	$p\text{-}NO_2\cdot C_6H_4\cdot OMe$
	SCN^- [i]	MeOH	$p\text{-}NO_2\cdot C_6H_4\cdot NMe_2$
	CN^- [d]	95% EtOH	$p\text{-}NO_2\cdot C_6H_4\cdot NMe_2$; MeCN; $p\text{-}NO_2\cdot C_6H_4\cdot OEt$ (a little)
	$HO\cdot C_6H_4\cdot O^-$ [d]	$(CH_2\cdot OH)_2$	$p\text{-}NO_2\cdot C_6H_4\cdot OH$; $p\text{-}NO_2\cdot C_6H_4\cdot NMe_2$
$CHPh_2\cdot NMe_3Br$ (I) [j]	CN^- [d]	$(CH_2\cdot OH)_2$ [k]	$CHPh_2\cdot O\cdot C_2H_4\cdot OH$; NMe_3; $CHPh_2\cdot NMe_2$; MeCN

[a] The figures reported are the relative proportions of products and not the degree of decomposition. When ethyl-alcoholic solutions of these quaternary salts were boiled for 10—12 hr. there was slight decomposition in the case of benzophenone-4 : 4′-bis(trimethylammonium iodide), a trace of Michler's ketone being formed; the other salts were recovered almost without decomposition. [b] This ketone was prepared [4a] by stirring, in an autoclave for 6 hr. at 90—100°, 4 : 4′-dihydroxybenzophenone and ethylene oxide in the presence of sodium methoxide in methanol, and from 4 : 4′-dihydroxybenzophenone and ethylene bromohydrin. [d] Yields are given in the Experimental part. [e] The nitrile is hydrolysed to the amide group before degradation of the quaternary ammonium group. Decomposition of the *p*-carbamoylphenyltrimethylammonium ion thus formed gave the products mentioned in the Table. [f] Decomposition of the iodide with 95% or absolute ethanolic sodium ethoxide confirmed this finding. [g] See also Hughes and Ingold.[5] We found that the iodide had m. p. 170—175° given by them; Sommelet (*Compt. rend.*, 1922, **175**, 1149) gave m. p. 205°. [h] Tadros and Latif, *J.*, 1949, 3337. [i] Tadros and Sakla, *J.*, 1954, 1116. [j] Zaki and Fahim, *J.*, 1942, 270. [k] Bolto and Miller, *Austral. J. Chem.*, 1956, **9**, 74.

* Part IV, *J.*, 1954, 1116.

XUM

The effect of causing the decomposition by 2-hydroxyethoxide instead of ethoxide may be related, at least in part, to a difference in electronic contribution (dipole moment [1] of ethanol, 1·691, 1·702, and of ethylene glycol, 2·28). The effect of the cyanide ion was similar to that of thiocyanate [2] on the decomposition of a trimethyl-*p*-nitrophenylammonium salt; Snyder and Speck,[3] however, report that benzyldimethylphenylammonium chloride was cleaved by boiling aqueous potassium thiocyanate solution but was unaffected under the same experimental conditions by sodium cyanide. A peculiar behaviour of the cyanide ion has been observed in other types of nucleophilic substitution.[4a] The cyanide ion in our reaction was not introduced into the benzene nucleus, although Beringer *et al.* showed that sodium cyanide reacted with 2- or 3-nitrodiphenyliodonium bromide to give the 2- or 3-nitrobenzonitrile.[4b]

Experimental

Diphenylmethanol, m. p. 68° [from light petroleum (b. p. 50—70°)], was obtained (*ca.* 65%) by reduction of benzophenone (200 g.) with sodium 2-hydroxyethoxide [from sodium (15·4 g.)] in ethylene glycol (330 c.c.) for 45 min. at the b. p.

Diphenylmethyl 2-Hydroxyethyl Ether.—Diphenylmethyl bromide [5] (10 g.) in ethylene glycol (30 c.c.) was warmed on the water-bath for 5 hr., then diluted with cold water (15 c.c.); the *ether*, obtained in almost quantitative yield and recrystallised from a little alcohol, had m. p. 69° (Found: C, 79·4; H, 7·0. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·0%).

4 : 4′-*Di*-(2-*hydroxyethoxy*)*benzophenone*.—Prepared from the sodium salt of the dihydroxyketone and ethylene bromohydrin by the standard method (4·28 g. of ketone; 1·15 g. of sodium; 30 c.c. of ethanol; 1 hour's refluxing), this compound had m. p. 167—168° (from alcohol) (Found: C, 67·7; H, 5·8. Calc. for $C_{17}H_{18}O_5$: C, 67·5; H, 6·0%). Caldwell [6] gave m. p. 174°.

Decomposition of Quaternary Salts.—(A) *Decomposition with potassium cyanide.* (*a*) Trimethyl-*p*-nitrophenylammonium iodide (3·08 g.) and potassium cyanide (1·95 g.) in 95% or absolute alcohol (30 c.c.) were refluxed. The solvent and methyl cyanide (identified as acetamide, m. p. and mixed m. p. 82°) were later distilled off and the residue was washed with water and recrystallised from alcohol. The product after 6 hours' heating was *NN*-dimethyl-*p*-nitroaniline (1·12 g.), m. p. and mixed m. p. 162—163°. Dilution of the alcohol mother-liquor gave a small quantity of *p*-nitrophenetole, m. p. and mixed m. p. 56—57°.

(*b*) A similar experiment (10 hr.) with *p*-cyanophenyltrimethylammonium iodide (2·88 g.) gave mainly *p*-dimethylaminobenzonitrile (1·16 g.), m. p. and mixed m. p. 76°.

(*c*) Diphenylmethyltrimethylammonium bromide [5] (3·06 g.) or iodide (3·53 g.) and potassium cyanide (1·95 g.) in ethylene glycol (30 c.c.) were heated on the water-bath for 10 hr. Trimethylamine was formed and identified as tetramethylammonium iodide, m. p. >230° (Found: I, 62·8. Calc. for $C_4H_{12}NI$: I, 63·2%). The ethylene glycol mother-liquor was diluted with water (15 c.c.) and extracted with ether. The extract was washed with dilute hydrochloric acid and evaporated. The residue, recrystallised from little alcohol, gave diphenylmethyl 2-hydroxyethyl ether m. p. and mixed m. p. 69°. The hydrochloric acid layer was neutralised with dilute aqueous sodium hydroxide. The diphenylmethyldimethylamine precipitated formed colourless crystals, m. p. and mixed m. p. 70°, from alcohol (picrate, m. p. and mixed m. p. 196°).

(*d*) Benzophenone-4 : 4′-bis(trimethylammonium iodide) (2·76 g.) and potassium cyanide (1·95 g.) in ethanol (150 c.c.) were refluxed for 6 hr., then diluted with cold water until precipitation was complete. Michler's ketone (0·6051 g., 45·2%), m. p. and mixed m. p. 172°, was obtained on recrystallisation from alcohol. When refluxing was for 10 hr., a trace of 4-dimethylamino-4′-ethoxybenzophenone, m. p. and mixed m. p. 108°, was also obtained.

(B) *Decomposition with sodium 2-hydroxyethoxide in ethylene glycol.* (*a*) Trimethyl-*p*-nitrophenylammonium iodide (3·08 g.) and sodium (0·46 g.) dissolved in ethylene glycol (25

[1] Conway, "Electrochemical Data," Elsevier Publ. Co., Amsterdam, 1952, pp. 14—15.
[2] Bolto and Miller, *J. Org. Chem.*, 1955, **20**, 558.
[3] Snyder and Speck, *J. Amer. Chem. Soc.*, 1939, **61**, 668.
[4] (*a*) Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 345; (*b*) Beringer, Brierley, Drexler, Cindler, and Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2708.
[5] Hughes and Ingold, *J.*, 1933, 69.
[6] Caldwell, U.S.P. (to Eastman Kodak) 2,675,411 and 2,675,367; *Chem. Abs.* 1954, **48**, 8262.

c.c.) were heated on the water-bath for 3 hr., then diluted with water, and the precipitate was treated with boiling water. The undissolved *NN*-dimethyl-*p*-nitroaniline (0·3 g.), recrystallised from alcohol, had m. p. and mixed m. p. 162—163°. The aqueous mother-liquor gave, on cooling, *p*-2-hydroxyethoxynitrobenzene (overall yield, 0·7 g.), m. p. and mixed m. p. 83—84°.

(*b*) Benzophenone-4 : 4′-bis(trimethylammonium iodide) (2·76 g.) and sodium (0·34 g.) dissolved in ethylene glycol (30 c.c.) were heated on the water-bath for 3 hr., then treated with hydrochloric acid (1 : 1), and the undissolved fraction was filtered off and recrystallised from alcohol to give 4 : 4′-di-(2-hydroxyethoxy)benzophenone (0·08 g.), m. p. and mixed m. p. 167—168°. On addition of aqueous sodium hydroxide to the acid filtrate, a small fraction, which from alcohol formed greenish-yellow crystals (0·06 g.), m. p. 128—129°, separated from the still acid medium. The acid mother-liquor was made alkaline, and Michler's ketone thus obtained recrystallised from alcohol (0·25 g.; m. p. and mixed m. p. 171°).

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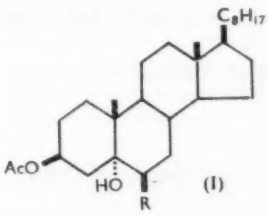
538. *A Second Carbonyl Band in the Spectra of Hydroxy-esters.*

By H. B. HENBEST, G. D. MEAKINS, and T. I. WRIGLEY.

THE formation of the fluorinated hydroxy-ester (I; R = F) from 3β-acetoxy-5α : 6α-epoxycholestane was reported recently.[1] The infrared spectra of solutions in CCl_4 and CS_2 of this compound and the corresponding chlorohydrin (I; R = Cl) are unusual in exhibiting two carbonyl bands, the expected acetoxyl band (1735 cm.$^{-1}$) being accompanied by a weaker band at lower frequency (1715 cm.$^{-1}$). However, in solutions of higher concentrations (see Table) the intensity of the 1715 cm.$^{-1}$ band increases while that of the 1735 cm.$^{-1}$ band decreases. The effect must thus be attributed to intermolecular association, the 1735 cm.$^{-1}$ peak representing non-associated acetoxyl (cf. the figures for 3α-acetoxycholestane) and the 1715 cm.$^{-1}$ absorption arising from acetoxyl groups involved in hydrogen-bonding between carbonyl oxygen atoms and hydroxyl groups. Although similar association is possible with 3β-acetoxycholestan-5α-ol (I; R = H) two carbonyl bands occur only at high concentration, and with the acyclic analogue, 3-acetoxypropan-1-ol, only one carbonyl band was present in the concentration range used with the steroidal hydroxy-acetates. The more pronounced tendency for bonding in the halogenohydrins is presumably due to the increased acidity of the 5-hydroxyl groups caused by inductive effects of the halogen atoms.



(I)

The hydroxyl regions of the steroidal hydroxy-acetates show non-associated and associated hydroxyl bands, the latter arising from hydroxyl–hydroxyl, hydroxyl–acetoxyl, or (less probably) hydroxyl–halogen association.[2,3] With the halogenated compounds (I; R = F and Cl) the bands of lower frequency are especially pronounced, indicating a marked contribution from the hydroxyl–acetoxyl bonding responsible for the double carbonyl absorption.

The qualitative effects of the intermolecular bonding of the halogenohydrins are similar to those already well established in spectroscopic studies of the association between hydroxyl and ester groups.[4] The unusual aspect is that the two carbonyl bands occur

[1] Henbest and Wrigley, *J.*, 1957, 4765.
[2] Henbest and Lovell, *J.*, 1957, 1965.
[3] Nickon, *J. Amer. Chem. Soc.*, 1957, **79**, 243.
[4] Searles, Tamres, and Barrow, *ibid.*, 1953, **75**, 71, and references cited therein.

XUM

Infrared frequencies (cm.$^{-1}$) of hydroxy-esters.

The compounds were examined in CCl_4 solutions (concentrations in mole/l.) on a Perkin-Elmer Model 21 spectrometer fitted with a calcium fluoride prism. Figures in parentheses are apparent molecular extinction coefficients in mole^{-1} l. cm.$^{-1}$. The intensity ratio of a pair of bands is the intensity of the higher-frequency band divided by that of the lower-frequency component.

	C=O Region			OH Region		
	Concn.	Bands	Int. ratio	Concn.	Bands	Int. ratio
3β-Acetoxycholestane *	0·0013	1734 (570)	—			
	0·01	1735 (555)	—			
3-Acetoxypropan-1-ol	0·0013	1745 (740)	—			
	0·01	1745 (730)	—			
3β-Acetoxycholestan-5α-ol (I; R = H) *	0·0013	1737 (550)	—	0·02	3615 (35)	0·9
	0·0051	1737 (570)	—		3465 (40)	
	0·01	1737 (510)	4·5			
		1718 (115)				
3β-Acetoxy-6α-chlorocholestan-5α-ol (I; R = Cl)	0·0013	1735 (515)	4·0	0·02	3605 (35)	0·6
		1718 (130)			3445 (60)	
	0·0052	1735 (460)	2·3			
		1715 (200)				
	0·01	1735 (415)	1·7			
		1715 (250)				
3β-Acetoxy-6β-fluorocholestan-5α-ol (I; R = F)	0·0013	1735 (545)	4·1	0·02	3610 (35)	0·6
		1718 (130)			3445 (60)	
	0·0052	1735 (500)	2·7			
		1715 (185)				
	0·01	1736 (460)	1·9			
		1715 (240)				

* Figures differ slightly from, and are more accurate than, those reported previously.[2]

at concentrations frequently used in routine examination of organic compounds. Thus the frequencies and relative intensities of the bands observed with 1% solutions might at first sight be taken to indicate the presence of an acetoxyl group and a keto-group in a six-membered ring.

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539. *The Possible Instability of Solid Anhydrous Argentic Nitrate.*

By D. F. C. MORRIS.

THE recent isolation of anhydrous cupric nitrate [1] has prompted a theoretical consideration of the possible stability of a solid argentic nitrate $Ag(NO_3)_2$. Noyes and his colleagues [2] have prepared solutions which must have contained the ions of argentic nitrate, but the solid is unknown.[3]

The standard molar free energy of formation of solid argentic nitrate at 25° can be estimated. This quantity, ΔG°_{298}, is related to the standard molar enthalpy of formation ΔH°_{298} and the standard molar entropies S°_{298} by the expression

$$\Delta G^\circ_{298}[Ag(NO_3)_2\,(s)] = \Delta H^\circ_{298}[Ag(NO_3)_2\,(s)] - 298{\cdot}2\{S^\circ_{298}[Ag(NO_3)_2\,(s)] - S^\circ_{298}[Ag\,(s)] - S^\circ_{298}[N_2\,(g)] - 3S^\circ_{298}[O_2\,(g)]\} \quad . \quad . \quad (1)$$

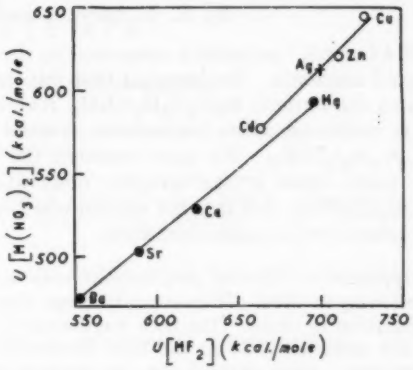
A knowledge of requisite enthalpy and entropy data will therefore permit the evaluation of the standard free energy of formation of the solid nitrate.

The standard molar enthalpy of formation of the compound can be derived by use of the equation

$$\Delta H^\circ_{298}[Ag(NO_3)_2\,(s)] = \Delta H^\circ_{298}[M^{2+}\,(g)] + 2\Delta H^\circ_{298}[NO_3^-\,(g)] - U \quad . \quad . \quad (2)$$

where U is the lattice energy (enthalpy) of the argentic nitrate at 25°. The data necessary for the calculation of $\Delta H^\circ_{298}[Ag(NO_3)_2\,(s)]$ from equation (2) are available [4,5] except for the value of the lattice energy. Kapustinskii [6] has derived various expressions for the

calculation of the lattice energies of electrovalent compounds of which the lattice constants are unknown. However, ionization potentials [7] suggest that argentic nitrate, if it existed, would have a high degree of covalent character. Therefore the use of Kapustinskii's equations does not appear to be suitable in the present case. Nevertheless, the lattice energy of $Ag(NO_3)_2$ can be estimated satisfactorily by use of various linear relations which exist between the "experimental" lattice energies of compounds of a given formula type.[8] Thus from the Figure the lattice energy of $Ag(NO_3)_2$ can be determined by interpolation, and the standard molar enthalpy of formation can then be derived.



Karapet'yants type of plot of the lattice energies of metal dinitrates and the lattice energies of corresponding difluorides.

In order to evaluate the standard free energy of formation from eqn. (1) it remains necessary to know the requisite standard entropies. These are available [4] except for $S°_{298}[Ag(NO_3)_2\ (s)]$ but this can be estimated by Latimer's method.[9]

The Table shows thermodynamic data for solid argentic nitrate and the standard enthalpy and free-energy changes for its most probable mode of decomposition. For comparison, values are quoted for solid anhydrous cupric nitrate. Where requisite data

Compound	$\Delta H°_{298}$ $[M^{2+}(g)]$ (kcal./mole)	$\Delta H°_{298}$ $[NO_3^-(g)]$ (kcal./mole)	U (kcal./mole)	$\Delta H°_{298}$ $[M(NO_3)_2\ (s)]$ (kcal./mole)	$S°_{298}$ $[M(NO_3)_2\ (s)]$ (e.u.)	$\Delta G°_{298}$ $[M(NO_3)_2\ (s)]$ (kcal./mole)
$Ag(NO_3)_2$ ...	740·7	−79·1	613	−31	48·2	15
$Cu(NO_3)_2$ ...	730·1	−79·1	645·3	−73·4	46·2	−27

$Ag(NO_3)_2\ (s) = AgNO_2\ (s) + NO_2\ (g) + \frac{1}{2}O_2\ (g)$; $\Delta H_{298} = 10$ kcal./mole; $\Delta G_{298} = -10$ kcal./mole; $(d\Delta G/dT)_p = -67{\cdot}4$ cal. deg.$^{-1}$.

$Cu(NO_3)_2\ (s) = CuO\ (s) + 2NO_2\ (g) + \frac{1}{2}O_2\ (g)$; $\Delta H_{298} = 53$ kcal./mole; $\Delta G_{298} = 21$ kcal./mole; $(d\Delta G/dT)_p = -104$ cal. deg.$^{-1}$.

are available [4,5] they have been used in composing the Table, otherwise magnitudes have been calculated as described here. It follows that the non-existence of a solid anhydrous argentic nitrate is in agreement with thermodynamic predictions.

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Brunel College of Technology, London, W.3. [*Received, February 19th*, 1958.]

[1] Addison and Hathaway, *Proc. Chem. Soc.*, 1957, 19.
[2] Noyes, Hoard, and Pitzer, *J. Amer. Chem. Soc.*, 1935, **57**, 1221; Noyes, Pitzer, and Dunn, *ibid.*, 1229; Noyes and Kossiakoff, *ibid.*, p. 1238; Noyes, Coryell, Stitt, and Kossiakoff, *ibid.*, 1937, **59**, 1316; Noyes, De Vault, Coryell, and Deake, *ibid.*, p. 1326.
[3] Sidgwick, "The Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, p. 175.
[4] Rossini, Wagman, Evans, Levine, and Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular of National Bureau of Standards, No. 500, 1952.
[5] Morris, *J. Inorg. Nuclear Chem.*, in the press.
[6] Kapustinskii, *Quart. Rev.* 1956, **10**, 283.
[7] Morris and Ahrens, *J. Inorg. Nuclear Chem.*, 1953, **3**, 263, 270; Morris, *J. Phys. and Chem. Solids*, in the press.
[8] Karapet'yants, *Zhur. fiz. Khim.*, 1954, **28**, 1136.
[9] Latimer, *J. Amer. Chem. Soc.*, 1951, **73**, 1480.

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540. *Preparation and Some Crystallographic Properties of Triamminoacetylenemagnesium Carbide* $MgC_2 \cdot C_2H_2 \cdot 3NH_3$.

By E. L. Lippert and Mary R. Truter.

In 1914 Cottrell [1] prepared a compound by the action of magnesium on acetylene dissolved in liquid ammonia. He reported that the transparent tetrahedral crystals, to which he assigned the formula $MgC_2 \cdot C_2H_2 \cdot 5NH_3$, reversibly lost ammonia at 0—2° to give a compound, stable at room temperature, partial analysis of which indicated the formula $(MgC_2 \cdot C_2H_2)_2 7NH_3$. We have repeated the preparation of the former compound and have made some crystallographic observations on it. We find its formula to be $MgC_2 \cdot C_2H_2 \cdot 3NH_3$, but it is not certain whether the ammonia and acetylene molecules are co-ordinated to the magnesium atom.

Experimental.—Several preparations were made with different amounts of magnesium by the following method. Magnesium turnings (0·01—0·10 g.) in a Pyrex tube were outgassed by heating them *in vacuo*. The tube was cooled to −176° and, after dry acetylene (0·16 g.) and then dry ammonia (0·35 g.) had been distilled in, it was sealed and allowed to warm to room temperature. After about 5 min., the solution evolved gas and deposited a white solid, which after several days at room temperature (still in the original sealed tube) was converted almost completely into transparent tetrahedral crystals, usually colourless but sometimes pale or dark brown. Unit cell dimensions of crystals of different colours were identical [Found, mean of three analyses: Mg, 19·4. Calc. for $(MgC_2 \cdot C_2H_2)_2 7NH_3$: Mg, 18·1. Calc. for $MgC_2 \cdot C_2H_2 \cdot 3NH_3$: Mg, 19·4%].

The crystals are stable in an atmosphere of dry ammonia at room temperature but with water give acetylene and magnesium hydroxide. Heating in dry ammonia gives magnesium amide which was identified by *X*-ray powder photographs. After storage *in vacuo* for 4 days, during which time the temperature rose from −70° to +20°, the crystals had decomposed to a cream-coloured powder which did not give a satisfactory *X*-ray powder photograph; this powder contained 35·1% of magnesium so that it may be impure $MgC_2 \cdot C_2H_2$ (cal.: Mg, 32·7%).

Single crystals were sealed into thin Pyrex capillary tubes in ammonia. They appeared isotropic under the polarising microscope and the cubic symmetry was confirmed by *X*-ray diffraction photographs. From a rotation photograph about [100] the unit cell edge was found to be $a = 16{\cdot}62 \pm 0{\cdot}02$ Å; density, found by flotation in benzene–chloroform, 1·06 g./c.c.; calculated for $24(MgC_2 \cdot C_2H_2 \cdot 3NH_3)$, 1·09 g./c.c.; calculated for $12[(MgC_2 \cdot C_2H_2)_2 7NH_3]$, 1·16 g./c.c.

X-Ray photographs taken at 20° and at −10° were identical. The crystal used was in the presence of ammonia and acetylene in the sealed Pyrex tube in which it had been made, conditions in which Cottrell found a reversible absorption of ammonia. Therefore, if a change in ammonia content takes place it is unaccompanied by a detectable change in crystal lattice.

Weissenberg photographs were taken of the 0th and 1st layer about the [100] axis and the 0th, 1st, and 2nd layer about the [101] axis. The only systematic absences were those for $(h00)$ with $h \neq 4n$ indicating that the space group is one of the enantiomorphic pair $P4_232(O^6)$ and $P4_132(O^7)$. (This is unexpected, the tetrahedral habit indicating a $\bar{4}$ axis, which would make the space group $P\bar{4}3m$ with no systematic absences.) No molecular symmetry is required by the space groups $P4_232$ or $P\bar{4}3m$, so that there are 3 parameters for each of 8 atoms (excluding hydrogen) to be determined. Unfortunately, because of the cubic symmetry and the high temperature factor the number of independent reflections (about 60) is insufficient for the determination of 24 parameters. No further work will be carried out on this compound at present.

We are grateful to Prof. E. G. Cox, F.R.S., and Dr. P. J. Wheatley for their interest.

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The University, Leeds 2. [*Received, March 3rd*, 1958.]

[1] Cottrell, *J. Phys. Chem.*, 1914, **18**, 85.